Interconversion of siloxanes

Thesis

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Interconversion of Siloxanes

A thesis submitted for the degree of

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By

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Statement

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- "Interconversion of Siloxanes," Bassindale, A.R., Taylor, P.G., Lane, T.H., Alvarez, K., Industrial & Engineering Chemistry Poster Session, ACS National Meeting, New Orleans, LA (March 2003) [Poster].
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- "All Acid Catalysts Used in Ring Opening Polymerisation of Cyclosiloxanes Are Not Created Equal," Bassindale, A.R., Taylor, P.G., Lane, T.H., Alvarez, K., Polymer Preprints, 45 (1), 568-569 (2004).
- "All Acid Catalysts Used in Ring Opening Polymerisation of Cyclosiloxanes Are Not Created Equal," Bassindale, A.R., Taylor, P.G., Lane, T.H., Alvarez, K., ACS National Meeting, Anaheim, CA (2004).
- "Acid Catalysed Interconversion of Cyclosiloxanes," Alvarez, K., Taylor, P.G., Lane, T.H., Bassindale, A.R., Organosilicon Symposium, Frankenmuth, MI (2006).

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Khris Alvarez

List of Abbreviations

2,6-*cis*	2,6-*cis*-diphenylhexamethylcyclotetrasiloxane
2,6-*trans*	2,6-*trans*-diphenylhexamethylcyclotetrasiloxane
DBMP	2,6-di-*tert*-butyl-4-methylpyridine
DBP	2,6-di-*tert*-butylpyridine
EBST	ethylboron sesquitriflate
GC	gas chromatography
GLC	gas/liquid chromatography
GPC	gel permeation chromatography
HMDZ	hexamethyldisilazane
IR	infrared
MS	mass spectroscopy
MW	molecular weight
NMR	nuclear magnetic resonance
PDMS	polydimethylsiloxane
$^{Ph}D_3$	2,4,6-triphenyl-2,4,6-trimethylcyclotrisiloxane
TMS	tetramethylsilane
TPFPB	tetrakis(pentafluorophenyl)borate
Triflic acid	trifluoromethanesulphonic acid
UV	ultraviolet
WERC	water exchange rate constant

Abstract

The acid catalysed interconversion of 2,6-diphenylhexamethylcyclotetrasiloxane in the presence of water was studied. Lewis and Brönsted acids were evaluated. Protic and aprotic solvents were used, as well as polar and nonpolar solvents. The interconversion of one stereoisomer of 2,6-diphenylhexamethylcyclotetrasiloxane (either 2,6-*cis* or 2,6-*trans*) to the equilibrium mixture of the two isomers occurs under the mild conditions of low temperature and weakly nucleophilic catalyst. Polymerisation becomes predominant under harsher reaction conditions (high temperature, high concentration of catalyst, strong nucleophile source).

Several findings were observed with the reactions of 2,6-diphenylhexamethyl-cyclotetrasiloxane. Interconversion is shown to be catalysed by both Lewis (e.g. iron chloride) and Brönsted (e.g. trifluoromethanesulphonic) acids in a polar aprotic solvent (e.g. nitromethane). The balance between interconversion and polymerisation can be controlled by temperature and catalyst acidity. Hydrochloric and nitric acid catalysts favour polymerisation, where interconversion conditions were found for trifluoromethanesulphonic and methanesulphonic acids. Only polar aprotic solvents were found to favour interconversion, which would support a separation of charge. No interconversion was observed with the nonpolar solvent pentane, while polymerisation was observed in the protic solvent *n*-butanol.

The study of this system has provided mechanistic insights for the acid catalysed interconversion of cyclosiloxanes, with implications for the mechanism of polymerisation. Common mechanistic steps are proposed for the acid catalysed interconversion and polymerisation reactions. A relatively low activation energy (approximately 16 kJ mol^{-1}) was determined for the interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane

catalysed by methanesulphonic acid. The activation energy for polymerisation of the same system was three times that of interconversion, approximately 40 kJ mol^{-1}.

Protonation of the cyclosiloxane oxygen, or possibly a metal complex coordination with the oxygen in the case of Lewis acid catalysis, is proposed as the first step of both reactions. Protonation is proposed as the essential requirement for the reaction, because the use of a proton sponge prevented both interconversion and polymerisation reactions. A large negative entropy of activation (in the order of -200 J mol^{-1} K^{-1}) was observed for all of the acid catalysed interconversion and polymerisation reactions studied of 2,6-diphenylhexamethylcyclotetrasiloxane. Nucleophilic attack at the silicon forms a pentacoordinate intermediate, and is consistent with a negative entropy of activation. The stability/ lifetime of this intermediate dictates the balance between interconversion and polymerisation products. Berry pseudorotations about the pentacoordinate silicon can occur if the intermediate is stable, or long-lived. Three consecutive rotations of the pentacoordinate silicon intermediate could result in stereoisomer interconversion after loss of the nucleophile, reforming a tetracoordinate silicon. Polymerisation ensues by siloxane bond breaking when the pentacoordinate silicon intermediate is less stable, or short-lived.

This work emphasises the mechanism for interconversion of asymmetric cyclosiloxanes in the presence of water, catalysed by acids. The control of this reaction might offer the explanation for the difficulty researchers have observed with acid catalysis of cyclosiloxanes to produce stereoregular siloxane-based polymers.

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Chapter One

Background and Scope

1 Background and Scope

1.1 Introduction

Siloxanes (commonly referred to as "silicones") are used in a wide range of products, from basic caulks and greases to personal care products and sophisticated medical and electronic devices. The industry had its beginnings in aviation applications during World War II, where silicone greases replaced pure organic materials because of their increased stability at high temperatures.[1] By 2003, the global market for siloxanes had grown to 7.8 billion U.S. dollars of sales per year.[2] Much of this market growth can be attributed to the unique alternating $(Si–O)_x$ repeat unit in the backbone of the siloxane polymer, which results in very desirable properties such as chemical and physical stability at high temperatures, high gas permeability, and low viscosity. Through the years researchers have attempted to uncover an alternative to the oxygen in the Si–O repeat unit of siloxanes, but nothing that results in the same variety of properties and chemical stability has been found.

The polymerisation of cyclosiloxanes has been an active area of research for many years. The importance of these silicon-based materials can be inferred from the maturing siloxane industry. In cyclosiloxanes the repeating Si–O units are assembled in a manner that forms linear or cyclic structures. Ring-opening polymerisation of cyclosiloxanes has been in use commercially since the 1940s as a nonequilibrium route to polymeric siloxanes. The molecular weight of the resulting polymer is controlled by the ratio of repeat units to end-capping units. The end-capping units act as a termination group as well as provide a means for introducing various organic groups to the polymer ends. Bases catalyse the ring-opening polymerisation of cyclosiloxanes, as do both protic (Brönsted) and nonprotic (Lewis) acids. The catalyst used for ring-opening must be

neutralised and/or removed to avoid subsequent redistribution that could ultimately produce an equilibrium mixture of linear and cyclic siloxanes.

Prior to the 1960s, organosilicon chemists considered siloxanes to be essentially biologically inert. In the late 1960s, mixed cyclosiloxanes [$(PhMeSiO)_x$ $(Me_2SiO)_y$] were shown to impart hormonal effects in rats.[3] Once isolated, each of the individual cyclosiloxane compounds in the mixture were found to be inactive except the isomer 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane (2,6-*cis*).[3] (The shorthand of "2,6-*cis*" and "2,6-*trans*" will be used to refer to the two possible isomers of 2,6-diphenylhexamethylcyclotetrasiloxane. The shorthand "2,4-isomers" refers to the isomers of 2,4-diphenylhexamethylcyclotetrasiloxane). The 2,6-*cis* isomer was found to impart estrogenic effects in rats and was evaluated in clinical trials as a potential cancer treatment. These trials were successful, but corporate financial support was limited. At the time this created a need for larger quantities of a pure form of the 2,6-*cis* isomer for human clinical trials. In the 1970s Frye and Spielvogel searched for a method to commercially produce pure 2,6-*cis* free of the 2,6-*trans*, and the 2,4 isomers. A distribution of isomers is formed during most methods of producing of this cyclosiloxane. The separation of the 2,6-*cis* from the 2,6-*trans* isomer was difficult, and thus costly, because of the close proximity of their boiling points and the decreased yield due to production of the other isomers.

Frye and Spielvogel went on to search for a technique that could convert 2,6-*trans* into 2,6-*cis* efficiently, and without by-products. They showed conditions where Lewis acids in polar aprotic solvents would convert either of the 2,6 isomers into an equilibrium mixture of the two without production of the expected 2,4 isomers and without the expected ring-opened products. They were unsuccessful in their attempts to interconvert the 2,6-*trans* isomer to the 2,6-*cis* isomer without producing other 2,4-isomers, using

Brönsted acids as catalysts.

To provide the chemical context for discussing these results and extensions of them documented in this report, this chapter briefly describes siloxane chemistry and nomenclature. A subsequent discussion of siloxane polymerisation covers ring-chain equilibrium and redistribution. The main focus of the chapter, however, is the ring-opening polymerisation of cyclosiloxanes. This provides the foundation for discussing the current research topic involving interconversion of stereoisomers of cyclosiloxanes (conversion from one stereoisomer to another).

Acidic conditions are typically used to convert cyclosiloxanes into polymers and other ring-opened products. Ring-opened products are expected under these conditions as they are quite similar to the parameters used to produce the ring-opened siloxane polymers sold in the silicone industry. The research discussed in this thesis demonstrates that acidic conditions also lead to the conversion of one stereoisomer of a cyclosiloxane to the other stereoisomer, *without forming any ring-opened by-products*. This finding provides new insight into the mechanism of polymerisation and highlights other reactions that may occur before and during polymerisation. A mechanism of this interconversion will be proposed, and implications discussed.

1.2 Siloxane Chemistry and Nomenclature

The element silicon represents approximately 28% of the earth's crust, but neither silicon, as the element, nor organosilicon compounds (where carbon is directly bonded to a silicon atom) exist naturally.[4] This is to say, that all of the silicon in the earth's crust is either in the form of silica or a mineral composite. Silicon metal is usually produced in an electric arc furnace by carbothermic reduction of mined quartz, a crystalline mineral form of silicon dioxide. There are two commonly used processes for the formation of Si–C

bonds, the Grignard process and the direct process. The two-step Grignard reaction for alkyl/aryl silane production was discovered by Kipping and Dilthey in 1904.[5,6] Organosilicon compounds can be produced from elemental silicon through what is known as the "direct process". Eugene Rochow and R. Müller are credited with discovery of the direct process in 1941, although Müller's patent was issued later.[7,8] As the name implies, the reaction adds organic groups to silicon in one step.

1.2.1 Grignard Process

The Grignard process uses organomagnesium compounds to transfer organic groups to silicon. The first step is the production of the Grignard reagent, which occurs by reaction of an alkyl or aryl halide with magnesium metal under an inert atmosphere. This organomagnesium compound is used in the second step to transfer its organic group to a silicon compound containing a good leaving group, commonly a chloride. In the organomagnesium compound the carbon-metal bond is a strong nucleophile and acts as a Lewis base toward the silicon. Commercially the Grignard process is used only when absolutely necessary because of the waste magnesium salt that is produced on a 1:1 mole ratio to every silicon molecule. This process is very costly due to the separation and disposal of this salt, but a much wider range of R– groups can be added to silicon with the Grignard process than with the direct process.

1.2.2 Direct Process

The direct process can be used to convert silicon into halosilanes by reaction of silicon metal with alkylhalides (e.g. CH_3Cl). Unfortunately, only methyl and phenyl halides are known to produce organofunctional silanes in reasonable yield. This reaction is typically catalysed by a complex mixture of metals consisting primarily of copper,

which produces a mixture of chlorosilanes (Figure 1.1), as well as organochlorohydridosilanes (e.g. $RSiHCl_2$, R_2SiHCl). The Si–H bond has a unique reactivity compared to the C–H bond and will be examined in the Section 1.2.4, Hydrosilylation.

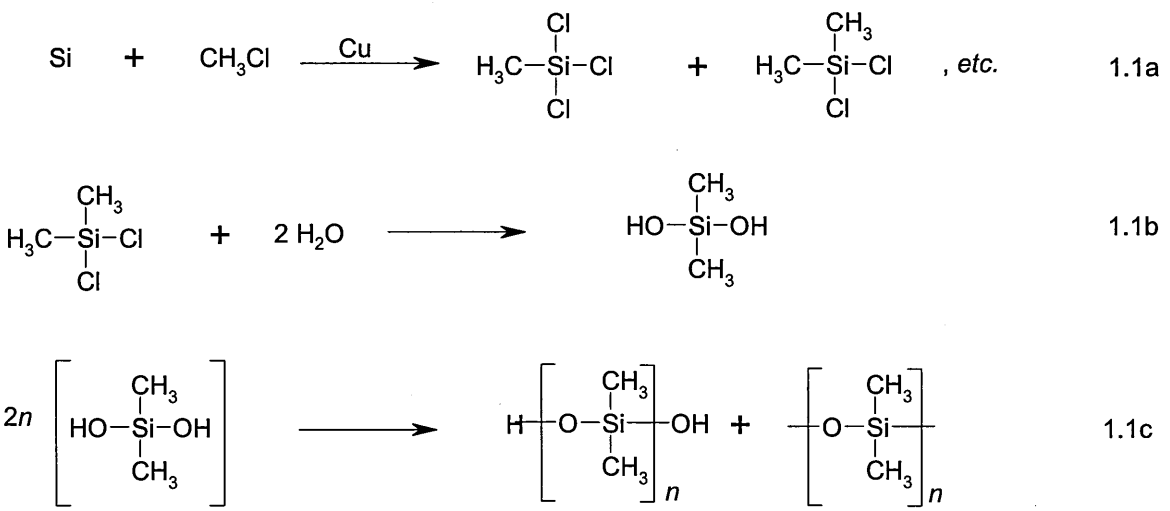


Figure 1.1 Production of chlorosilanes by the direct process (1.1a), hydrolysis of chlorosilanes (1.1b), condensation of silanols to produce linear and cyclic siloxanes (1.1c)

The mechanism of the direct process is not yet fully understood and continues to be an active area of research. The reaction mechanism was once thought to involve radicals, but this would not account for all of the by-products, which can include more than 40 compounds. A silylene insertion mechanism has more recently been proposed, where SiX_2 is inserted into HX (see Figure 1.2).[9]

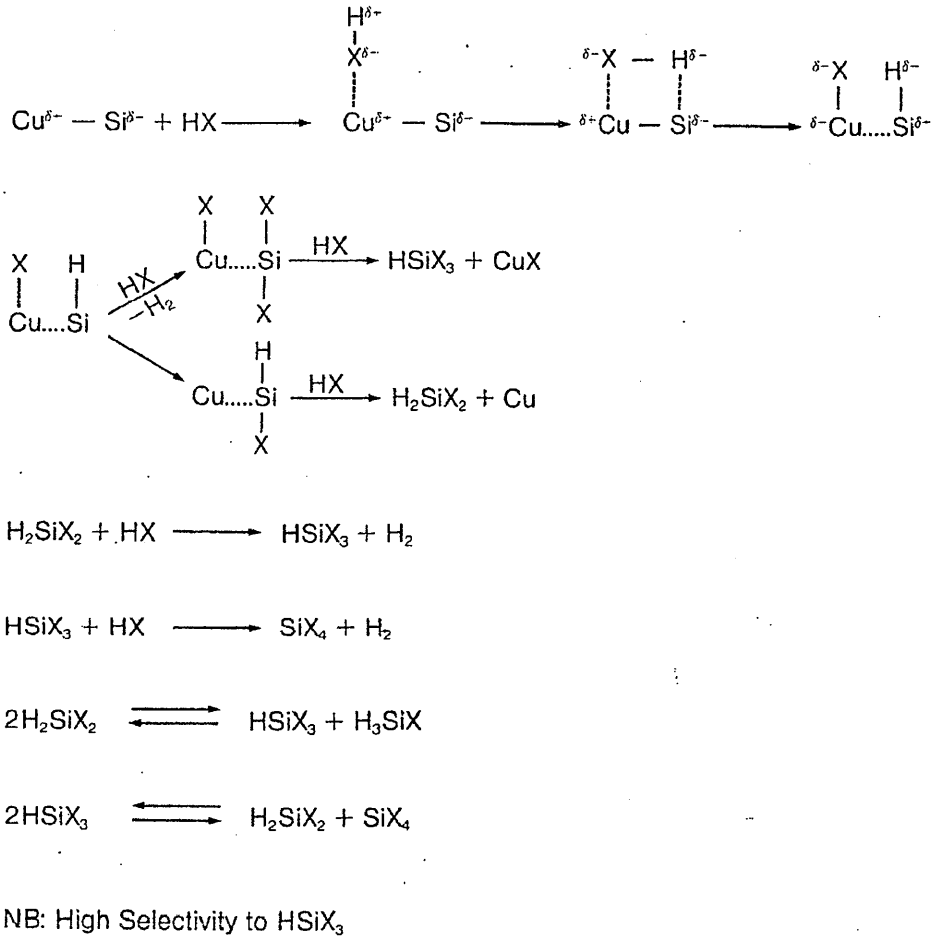


Figure 1.2 Recently proposed direct process mechanism (where X= OCH_3, OC_2H_5, $N(CH_3)_2$, Cl, Br)

*Reprinted from: Falconer; Frank; Kanner; McLeod; Lewis, Surface-Chemical Studies of the Mechanism of the Direct Synthesis of Methylchlorosilanes. In Catalyzed Direct Reactions of Silicon; Elsevier: **1993**; pp 333-441, with permission.*

Much of the mechanistic research has been carried out by industry and is held as a trade secret due to the importance of the resulting chlorosilanes as key building blocks for the silane/silicone industry.

These chlorine-functional silanes are separated by fractional distillation and used as various building blocks depending upon their functionality. The chlorine atoms on silicon are good leaving groups and thus the number of chlorine atoms can be viewed as the amount of functionality or number of reactive sites a silicon atom possesses.

1.2.3 Hydrolysis/Condensation

After separation the difunctional organodichlorosilanes are allowed to react with water, and silanols are formed with release of hydrogen chloride (Figure 1.1b). These silan*ols*, unlike analogous carbon-based alcoh*ols*, are not very stable under ambient conditions and readily undergo condensation to form linear and cyclic siloxanes (Figure 1.1c), releasing water as part of the reaction. The final composition depends on the reactants used, where difunctional (R_2SiCl_2) compounds increase the chain length, and monofunctional (R_3SiCl) materials cap the polymer chain. The yield of cyclosiloxanes increases with aqueous HCl. Bases, such as KOH, can be added to maintain neutral pH to lead to more linear siloxanes. The equilibrium induced by acid and base catalysts is a result of redistribution of the ring and chain siloxanes formed and will be examined further in Section 1.3 Ring-opening Polymerisation. The addition of organohalosilanes to an excess of an alkaline solution usually leads to high molecular weight siloxane polymers because such excess alkalinity accelerates hydrolysis.[10] The solvent choice can impact the distribution between linear and cyclic siloxane formation under both acidic and basic conditions. The use of solvents that are immiscible with water increases the yield of cyclosiloxanes. Such solvents dilute the siloxane phase, thus shifting the equilibrium toward intramolecular condensation of intermediate diols, with formation of cyclics. This is discussed further in Section 1.3.1 Ring-Chain Equilibria.

The rate of hydrolysis in Figure 1.1b depends on the steric hindrance at the silicon centre, polarity and the concentration of silicon halide bonds. Bulky groups on silicon sterically hinder nucleophilic attack on the Si, thus retarding hydrolysis. Electron donating substituents on the silicon atom (e.g. phenyl) strengthen neighbouring Si–Cl bonds because these substituents (i.e. phenyl) donate electron density back to the silicon to compensate for the electron density pull from the chloride atom. These stronger bonds are

much less reactive to water, thus hydrolysis is hindered. For example, methylphenyldichlorosilane is more difficult to hydrolyse than dimethyldichlorosilane due to the size and electronegativity of the phenyl groups.

1.2.4 Hydrosilylation

As discussed earlier, no naturally occurring compounds with Si–C bonds have been discovered. Hydrosilylation is another useful method of forming Si–C bonds, and without the manufacture of by-products. Hydrosilylation is an addition reaction of Si–H to a multiple bond (π-bond), i.e. C=C or C≡C to form a Si–C bond. The reactivity of the Si–H bond is different from the C–H bond because the electronegativity of silicon is lower than both carbon and hydrogen. A covalent $Si^{\delta+}$–$H^{\delta-}$ bond is opposite in polarity from that of a $C^{\delta-}$–$H^{\delta+}$ bond, making Si more suitable to nucleophilic attack. Radicals, heat, and transition metal (e.g. Pt, Pd, Rh, Ru, Co, Ni, Ir, Fe, Os) catalysts have been shown to initiate the addition reaction. In 1957 John Speier discovered chloroplatinic acid (H_2PtCl_6) to be more efficient than supported catalysts (e.g. platinum on carbon).[11] This reaction can be carried out in solution or neat using only a small amount of catalyst (often <1 ppm) and is often exothermic. Addition to the C=C double bond predominately occurs in an anti-Markovnikov fashion with the silicon adding to the carbon with more hydrogen atoms. Chalk and Harrod proposed an early mechanism for the transition-metal-catalysed hydrosilylation of alkenes based on other transition-metal-catalysed reactions, see Figure 1.3.[12]

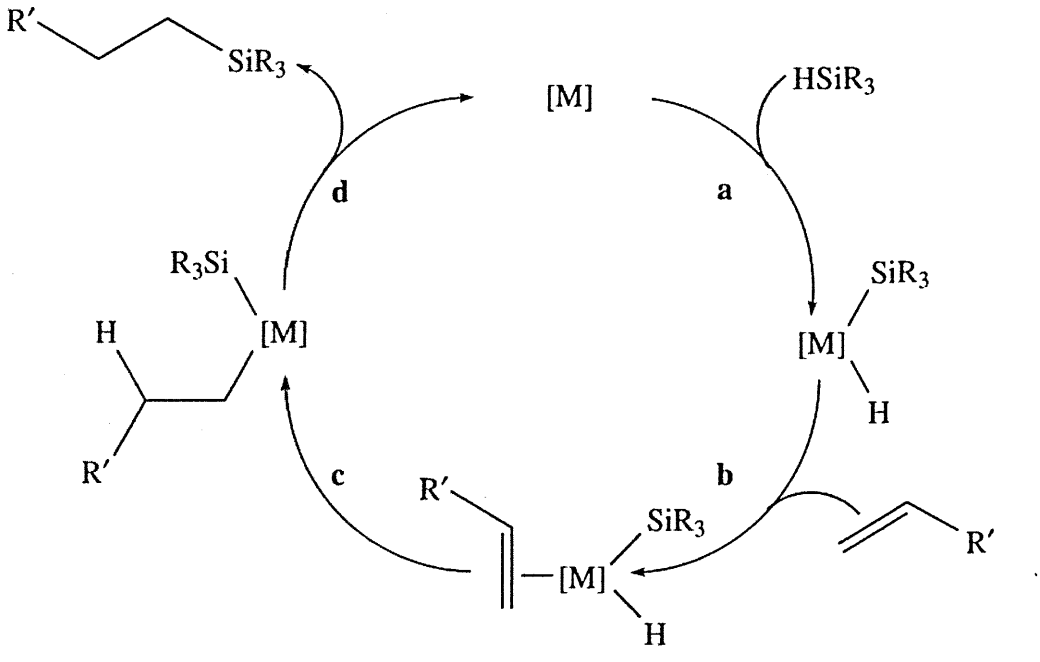


Figure 1.3 Chalk-Harrod mechanism for hydrosilylation

*Reprinted from: Ojima, I.; Li, Z.; Zhu, J., Recent Advances in the Hydrosilylation and Related Reactions. In The Chemistry of Organic Silicon Compounds, Rappoport, Z.; Apeloig, Y., Eds.; John Wiley & Sons: Chichester, **1998**; Vol. 2, pp 1687-1792, with permission.*

The Chalk-Harrod mechanism inserts the unsaturated bond (Figure 1.3, step b) into the metal-hydrogen bond (formed in step a).[13] The Chalk-Harrod mechanism cannot explain the differences observed between catalyst systems (i.e. platinum versus cobalt), and several silyl migration pathways have been proposed, see Figure 1.4.[12]

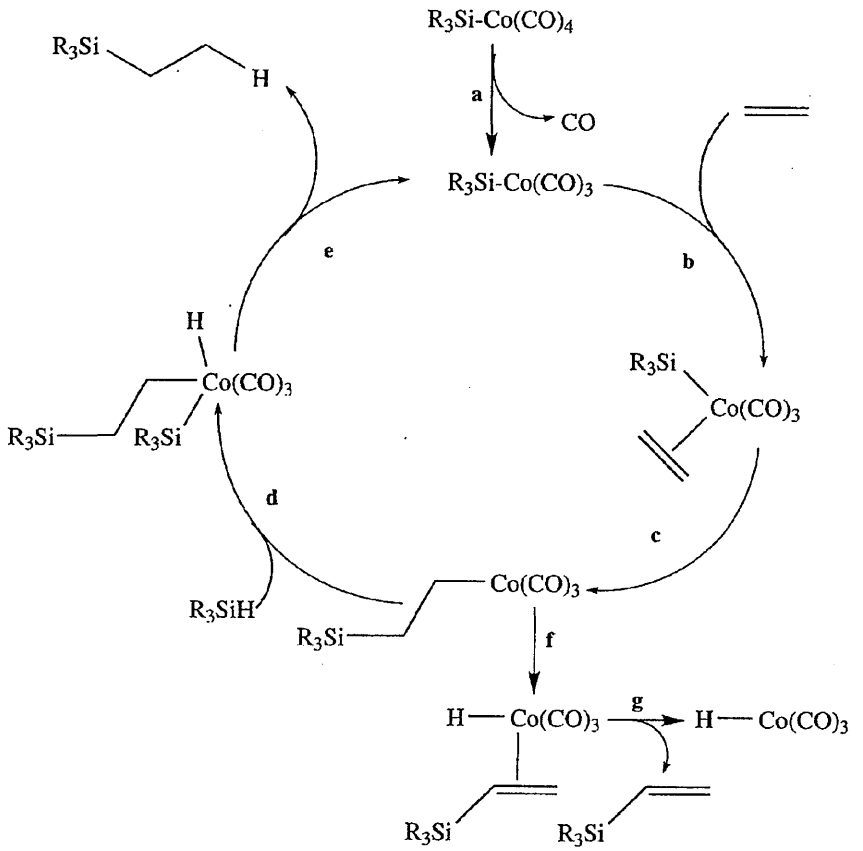


Figure 1.4 Proposed silyl migration mechanism for hydrosilylation by Seitz and Wrighton

*Reprinted from: Ojima, I.; Li, Z.; Zhu, J., Recent Advances in the Hydrosilylation and Related Reactions. In The Chemistry of Organic Silicon Compounds, Rappoport, Z.; Apeloig, Y., Eds.; John Wiley & Sons: Chichester, **1998**; Vol. 2, pp 1687-1792, with permission.*

The Seitz-Wrighton mechanism in Figure 1.4 inserts the alkene into the metal-silicon bond, instead of the metal-hydrogen bond as in the Chalk-Harrod mechanism. The hydrosilylation reaction and its mechanism continue to be very active research subjects.

1.2.5 Si–O versus C–C

There are some interesting facts regarding the siloxane (Si–O) bond that highlight differences compared to a carbon-carbon bond. These insights help explain the reactivity as well as some of the unique properties of siloxane polymers, such as low glass transition temperature (~ –120°C), low viscosity, high gas permeability, hydrophobicity, and high

thermal stability. The siloxane-based polymer contains a longer bond length between backbone atoms and a wider bond angle compared to a polymer containing a carbon backbone. The lack of side groups on the oxygen imparts a low barrier to rotation about the bonds, resulting in low intermolecular forces. This helps explain the low glass transition temperature.

The flexibility of a Si–O bond is even more interesting in light of the high strength of the bond. The energy required to break the Si–O bond is ~100 kcal/mole; the C–C bond energy is 85 kcal/mole.[1] Thus, the siloxane backbone is more flexible yet stronger than that of a carbon-based polymer and is the reason for siloxane's higher thermal stability.

Silicon and carbon are typically tetravalent since they are members of Group 14 in the periodic table. Silicon is atomically larger (1.17 Å) than carbon (0.77 Å), and it is less electronegative.[14] This produces more polar Si–X bonds compared to C–X with most X's. Through the 1960s the unusually strong silicon-halogen bond was attributed to backbonding of the lone-pair of electrons on the halogen to the silicon atom, forming a pseudo π-bond. For many years it was thought this backbonding took place from the lone pair electrons of the halide into the vacant *d*-orbitals of the silicon. The similar electronegativity of carbon and sulphur (Pauling electronegativity of 2.55 versus 2.58) may explain why Si–C and Si–S bond strengths are similar even though the lone pair of electrons on sulphur is available for backbonding, yet not possible with carbon.[15] There are cases where neither of the backbonding theories explains the bond strengths observed with some silicon-element bonds. Recently ab initio calculations suggest the σ^*-orbitals are of more correct symmetry to receive the backbonding electrons.[4] These orbitals are available because of their low energy due to the electronegativity of silicon.

The bond length of a silicon-oxygen bond at 1.65 Å (in

octamethylcyclotetrasiloxane) imparts more flexibility than that observed in a carbon-carbon bond with a length of 1.54 Å (in CH_3CH_3).[16] The average bond angle of Si–O–Si is 130° to 160°, while a bond angle of only 109.5° is observed for C–C–C. The Pauling electronegativity of silicon is 1.90, and that of oxygen is 3.44. A difference of 2.0 or more is typically considered ionic. This moderate difference in electronegativity produces a siloxane bond that although covalent, has some ionic nature. Silicon's larger atomic size also decreases the barrier to bond rotation compared to carbon.[16] The large radius of the silicon atom combined with a large Si–O–Si bond angle allows the linear Si–O backbone of the polymer to form a twisted, and even a helix-type structure has been proposed, with the alkyl substituents projecting outward.[1] Thus, the polymer appears mostly organic to its surroundings and contributes to the nonpolar and hydrophobic nature of the polymer. The most stable conformation of PDMS is described as *cis-trans* according to ab initio molecular calculations.[17] This is shown in Figure 1.5.

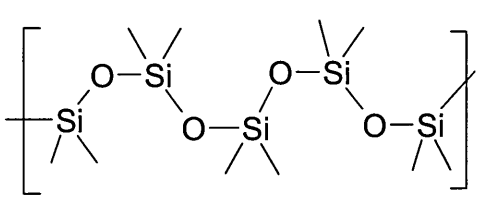


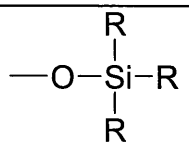
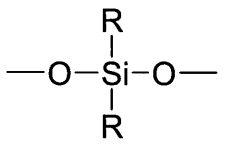
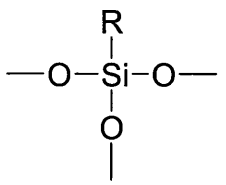
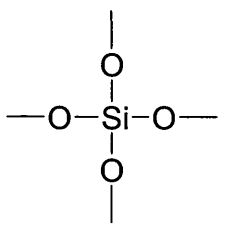
Figure 1.5 Proposed *cis-trans* conformation of polydimethylsiloxane by Grigoras[17]

Computational modelling carried out in the late 1980s suggests that (p-d) π bonding is not a valid concept for the bending flexibility of the Si-O-Si angle (140-180°).[18, 19] The electronic charge from the lone pair on oxygen is transferred to the covalent bonding region between silicon and oxygen.[20] This diminishes the lone pairs on oxygen and alters the sp^3 hybridised geometry. The authors used disiloxane and hexamethyldisiloxane as model systems using the modified 3-21G* basis set. Grigoras and Lane suggest this charge transfer widens the Si-O-Si angle and the additional charge in the covalent region shortens the Si-O bond length.

Carbon rarely expands its coordination number beyond four, but silicon can expand its coordination number more easily because it contains vacant *d*-orbitals in addition to the s- and p-orbitals that carbon has; this is discussed further in Section 1.5, Pentacoordinate Si. Conversely, silicon rarely forms multiple bonds, but this is common for carbon. The larger size of silicon versus carbon leads to less stable π-bonds. Kipping first suggested the term "silicone" as a generic descriptor for a molecule containing a silicon-oxygen bond (Si–O), also known as siloxane, because the molecule was originally thought to be a silicon double-bonded to oxygen (Si=O).[1] The term silicone can be misleading when compared to ketone because the Si=O double bond is unstable. The other bonds to silicon can be methyl groups, which can be formed from chloromethane gas as shown in Figure 1.1a above. A polymer prepared from repeating $(Si–O)_x$ units is generally referred to as a silicone, but a more specific name for the siloxane polymer produced from condensation in Figure 1.1c is polydimethylsiloxane (PDMS). The following section provides more specific details on nomenclature.

1.2.6 Nomenclature

The General Electric shorthand nomenclature of M, D, T, and Q is generally accepted for siloxanes. The letter designation represents each silicon unit distinguished by the number of oxygen atoms bonded to the silicon, where M = mono, D = di, T = tri, and Q = quad, with 1, 2, 3, and 4 oxygen atoms, respectively, bonded to a silicon atom, see Figure 1.6.[1]

Nomenclature	Structure
M	
D	
T	
Q	

R = CH_3, unless otherwise specified

Figure 1.6 Siloxane shorthand nomenclature

When more than one silicon atom of the same type (M, D, T, or Q) is present in the same structure, it is denoted by a subscript. For example, M_2 (or MM) represents hexamethyldisiloxane using this shorthand. If other groups bonded to silicon are not specifically named, they are assumed to be methyl (CH_3). When groups other than methyl are used, they are denoted by a superscript. For example, $^{Ph}D_3$ represents $(PhSiMeO)_3$, where one methyl on each silicon atom has been replaced with a phenyl group (Figure 1.7).

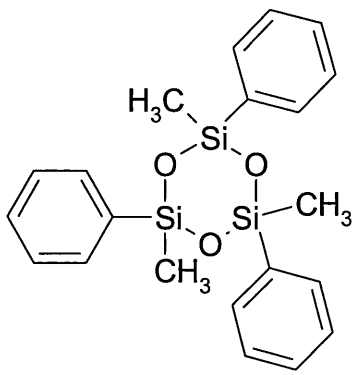


Figure 1.7 2,4,6-Triphenyl-2,4,6-trimethylcyclotrisiloxane, $^{Ph}D_3$

The most common cyclic structures produced from the hydrolytic polycondensation of chlorosilanes are D_3, D_4, and D_5. Due to ring strain, D_3, a six-member ring, is the smallest cyclic siloxane observed under typical conditions. These small cyclic materials form the building blocks for siloxane polymers produced by ring-opening polymerisation.

1.3 Ring-opening Polymerisation

As discussed in the introduction to this chapter, siloxane polymers can be formed by condensation of silanols or ring-opening of cyclic molecules containing Si–O bonds that form repeat units. Ring-opening polymerisation of purified cyclosiloxanes is typically the method used to produce high MW (molecular weight) siloxane polymers, because direct hydrolysis of chlorosiloxanes can leave behind unwanted chlorosilane impurities. The majority of high MW siloxane polymers are produced by ring-opening polymerisation, a chain growth process of cyclosiloxanes (cyclic siloxanes, or cyclics), typically D_3, D_4 (Figure 1.8), and D_5.

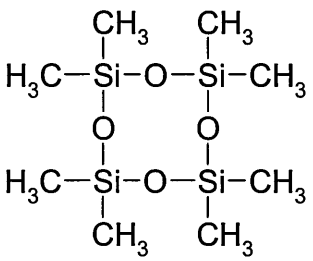


Figure 1.8 Octamethylcyclotetrasiloxane (D_4).

Hyde was the first to patent a process for ring-opening polymerisation of cyclosiloxanes.[21,22] In principle, this is an equilibrium reaction that produces a thermodynamically controlled mixture of cyclic and linear siloxanes. In practice, however, the reaction is a kinetic polymerisation controlled by choice of monomer, initiator, and other conditions. Ring-opening polymerisation of cyclics grows the chain by opening D_x (depending on the starting materials) cyclic units initially, followed by redistribution.[23] The MW is controlled by the amount of end-capper, which typically is introduced in the form $R_3SiOSiR_3$. Factors such as the size and type of the R groups attached to silicon and the size of the ring influence the rate of polymerisation and the position of the equilibrium. Intramolecular cleaving reactions of the growing polymer chains can produce smaller linear chains and cyclics, where the reactive chain end groups react internally to produce smaller molecules instead of reacting with another molecule to increase the MW. These "back-biting" reactions lead to a statistical distribution of chains and cyclics which can be biased by the reaction conditions and the starting materials used. This secondary redistribution reaction is shown in a viscosity vs. time plot of the polymerisation of a cyclosiloxane, Figure 1.9. The viscosity steadily increases during the addition of D_x units, then drops during the later redistribution process.[24]

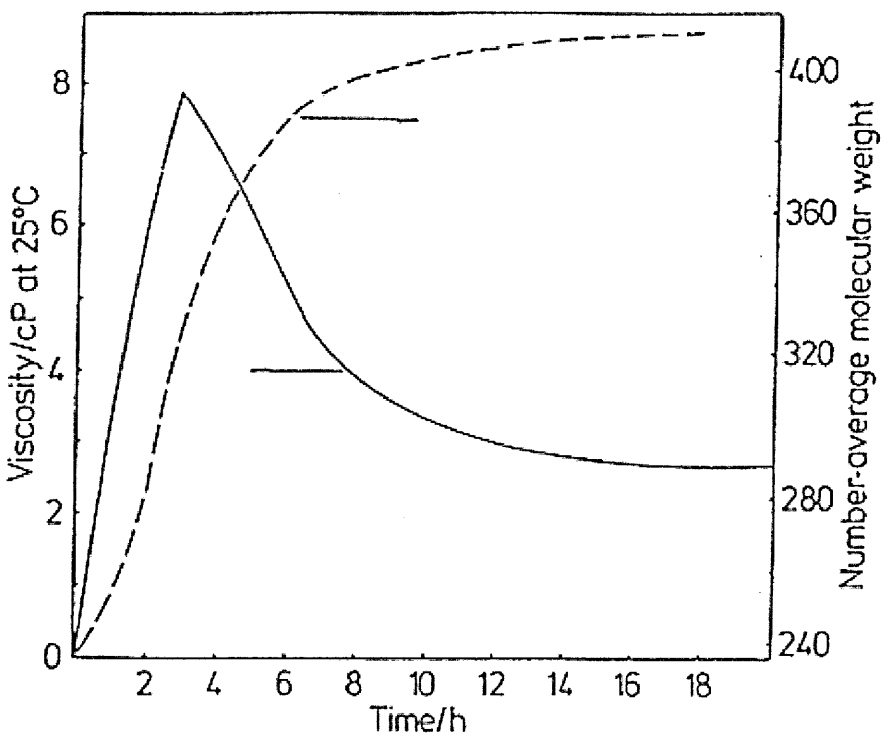


Figure 1.9 Change in viscosity (solid line) and number average MW (dashed line) versus time for polymerization of D_4 with MM and 0.1% Me_4NOH at 80°C

Reprinted from: Wright, P. V., Cyclic Siloxanes, Chapter 14. In Ring Opening Polymerization, K. J. Ivin, T. S., Ed.; Elsevier: ***1984****; Vol. 2, with permission.*

The redistribution of siloxane polymers tends to occur when there is acid or base catalyst remaining from the polymerisation process that has not been sufficiently neutralised. In acid polymerisation, only strong acids open cyclosiloxane rings, and so typically weak bases are used to neutralise the catalyst. In the same way, relatively strong bases are necessary to induce polymerisation, and thus weak acids are neutralizing agents. The residual acid or base will attack Si–O units until an equilibrium mixture is obtained with a Gaussian (statistically normal) distribution of MW.

1.3.1 Ring-Chain Equilibria

Most processes used to produce high MW siloxane polymers form a MW distribution of linear polymers and a distribution of cyclosiloxanes. The equilibrium position of the distribution between ring (cyclic) and chain siloxanes, known as "ring-chain equilibria", can be affected by several parameters (catalyst, solvent, thermodynamics, R group, etc.).

Scott was the first to show production of cyclics other than the D_4 starting material during acid-catalysed polymerisation.[25] Soon thereafter gas/liquid chromatography (GLC) and gel permeation chromatography (GPC) were used to separate and quantify the range of cyclic and linear siloxanes formed by acid- or base-catalysed ring-opening polymerisation of cyclosiloxanes. Carmichael and Winger showed that the position of the ring-chain equilibrium is independent of temperature in the range of 25 to 178°C, as well as independent of the catalyst (potassium silanolate (1 K/5000 Si) and 5% sulphuric acid by weight).[26] The Jacobson-Stockmayer theory can be used to predict the cyclic content in these systems.[27] Ring-chain equilibration between siloxane rings D_x and polymeric chains D_n and D_{n-x} can be represented by the following equation:[28,29]

$$D_n \rightleftharpoons D_{n-x} + D_x$$

and the equilibrium constant K_x:

$$K_x = \frac{[D_{n-x}][D_x]}{[D_n]} = \frac{[D_x]}{p^x}$$

where $[D_x]$, $[D_{n-x}]$, and $[D_n]$ represent the concentration of cyclic products, linear products, and polymer reactant (typically cyclics for siloxanes), respectively. Also, x and n are degrees of polymerisation, and p is the extent of reaction of functional groups in the chain

fraction of the equilibrate, i.e. non-terminal groups. When cyclic molecules are not too large at equilibrium, p is close to 1, causing $K_x \cong [D_x]$. The Jacobson-Stockmayer cyclisation theory predicts the following relationships for the cyclisation constant of large cyclosiloxanes (approximately 20 or more repeat units):[30]

$$K_x = \left(\frac{3}{2\pi (r_x)^2} \right)^{3/2} = \left(\frac{1}{N_A (2_x)} \right)$$

where (r_x^2) is the mean-square end-to-end distance of the siloxane chains (one Si–O unit equates to 1.64×10^{-8} cm), N_A is Avogadro's number, and 2_x is the symmetry number (number of chain atoms in the repeat unit, Si–O = 2).

This relationship is based on several assumptions. First, the enthalpy change between linear and cyclosiloxanes must be zero. This is true for unstrained rings, but not for D_3 because there is ring strain in this structure and thus the enthalpy change during ring-opening is not zero. Another assumption used in this equation is that the distribution of siloxane chains must obey a Gaussian statistical distribution. The final assumption is that the chains must be oriented in a random fashion.

Semlyen and Wright compared the Jacobson-Stockmayer computed data with experimental results and found the equilibrium constant (K_x) to be independent of dilution for larger rings, where x = 11 to 40.[31] K_x increases with dilution for smaller cyclic molecules, where x = 4 to 10. Of most importance, there is a concentration for a given solvent starting cyclic material combination below which the equilibrium product is entirely cyclics for these smaller rings, see Figure 1.10.[28]

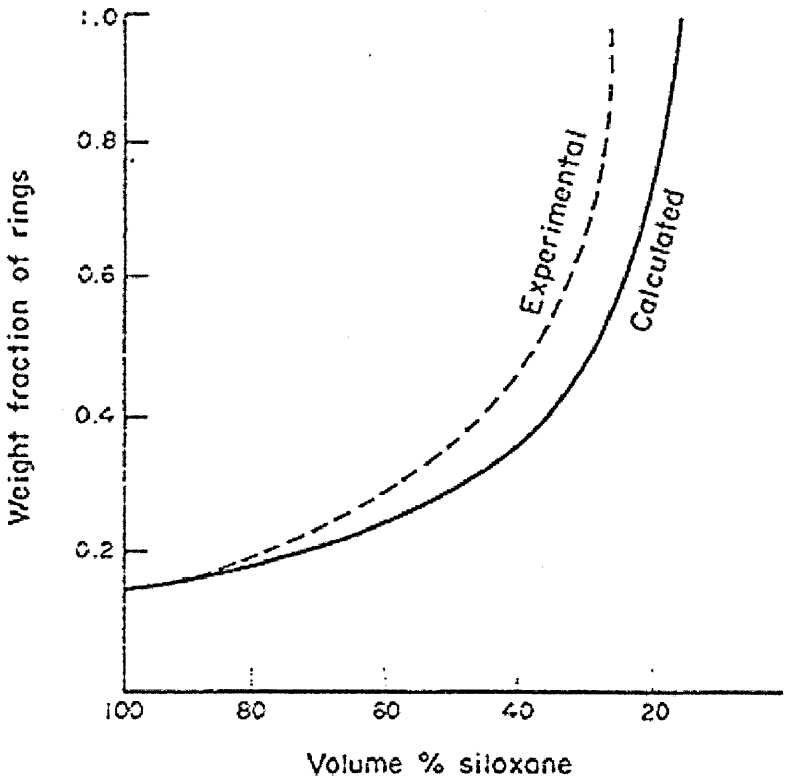


Figure 1.10 Weight fraction of cyclics in PDMS equilibrates as a function of solvent dilution

*Reprinted from: Kendrick, T. C.; White, J. W.; Parbhoo, B., Polymerization of Cyclosiloxanes. In Comprehensive Polymer Science, G. C. Eastmond, A. L., S. Russo, P. Sigwalt, Ed.; Pergamon Press: **1989**; Vol. 4, pp 459-523, with permission.*

As the cyclic concentration decreases, intermolecular interactions decrease, relative to intramolecular interactions, and thus more cyclics are produced. The experimental deviation from the calculated values in Figure 1.10 occurs because smaller polymers do not obey Gaussian statistics as assumed in the model. To maximise the distribution of linear polymer versus cyclic molecules in an equilibrating mixture, ring-opening polymerisation must be practiced in as concentrated a solution as practical.

When one of the R groups is varied on each silicon of a D_x cyclic starting material, the position of the resulting ring-chain equilibrium can be drastically shifted. More cyclics are observed as the R group becomes more bulky (steric interactions) or more

polar. The polar group may cause more interaction within the chain and decrease the chain mobility of the polymer, causing an entropy decrease and thus disfavour chain formation. In the same way, large groups may also reduce the chain mobility. The equilibrium cyclic content increases, as shown in Figure 1.11, in the order R = H < CH_3 < CH_3CH_2 < C_6H_5 < $CF_3CH_2CH_2$.[32 33] Thus, polymerisation of cyclics, especially where R = $CF_3CH_2CH_2$, must be carried out under nonequilibrium conditions to produce a high yield of linear polymer.

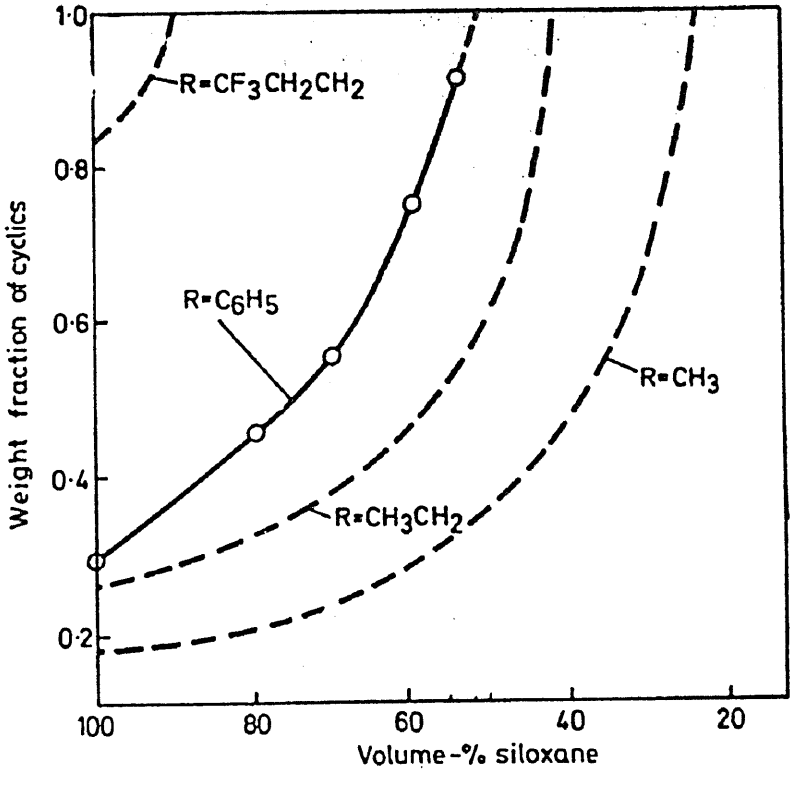


Figure 1.11 Weight fraction of cyclics $[R(CH_3)SiO]_x$ in high molecular weight ($p \simeq 1$) polysiloxane equilibriates at 383 K as a function of volume percent siloxane in toluene (R=C_6H_5, CH_3CH_2, CH_3) and cyclohexanone (R=$CF_3CH_2CH_2$)

Reprinted from: Beevers, M. S.; Semlyen, J. A., Polymer ***1971,*** *12, p 373, with permission (license 1764260625909).*

Experimental data for siloxane polymer chains containing more than 15 bonds obey Gaussian statistics and the Jacobson-Stockmayer theory.[34-38] For smaller siloxanes,

where $x < 16$, there is not good agreement between the experimental and calculated results. This indicates that these smaller siloxanes do not obey Gaussian statistics and/or do not have randomly oriented chain ends. However, Beevers and Semlyen showed that values of K_8 and K_9 are in good agreement with experimental results for the concentrated equilibrate.[35] Scales and Semlyen found good agreement with K_{10}, as well, but K_{11} deviated by a factor of 3.[39] The authors draw attention to the limit of the model caused by using fixed bond angles at oxygen and having only three rotational states. Flory and Semlyen found satisfactory results for K_5, K_6, and K_7 with a slight modification of the rotational isomeric state model.[40-43] Thus the model fits the experimental results fairly well with some limitations and can be used as a predictive tool.

Several excellent reviews of siloxane polymerisation have been written and include a more detailed discussion of ring-chain equilibria.[24, 28, 44, 45]

1.3.2 Base-catalysed Polymerisation

Acidic or basic catalysts can affect ring-opening polymerisation, but each occurs through a different mechanism. Anionic (base-catalysed) polymerisation of cyclosiloxanes is fairly well understood, although there is disagreement regarding the active catalytic species. Initiation of base-catalysed polymerisation involves nucleophilic attack of the base on a silicon atom of a cyclosiloxane (the –OH attacks the Si atom in Figure 1.12 to produce a ring-opened silanolate). Both anionic- and cationic-catalysed polymerisation can have characteristics of a living polymerisation. In a living polymerisation, the propagating centre does not undergo termination or transfer.[46] The reaction does not have a termination step, the active ends (e.g. silanolate) must be neutralised or capped, to avoid redistribution to an equilibrium.

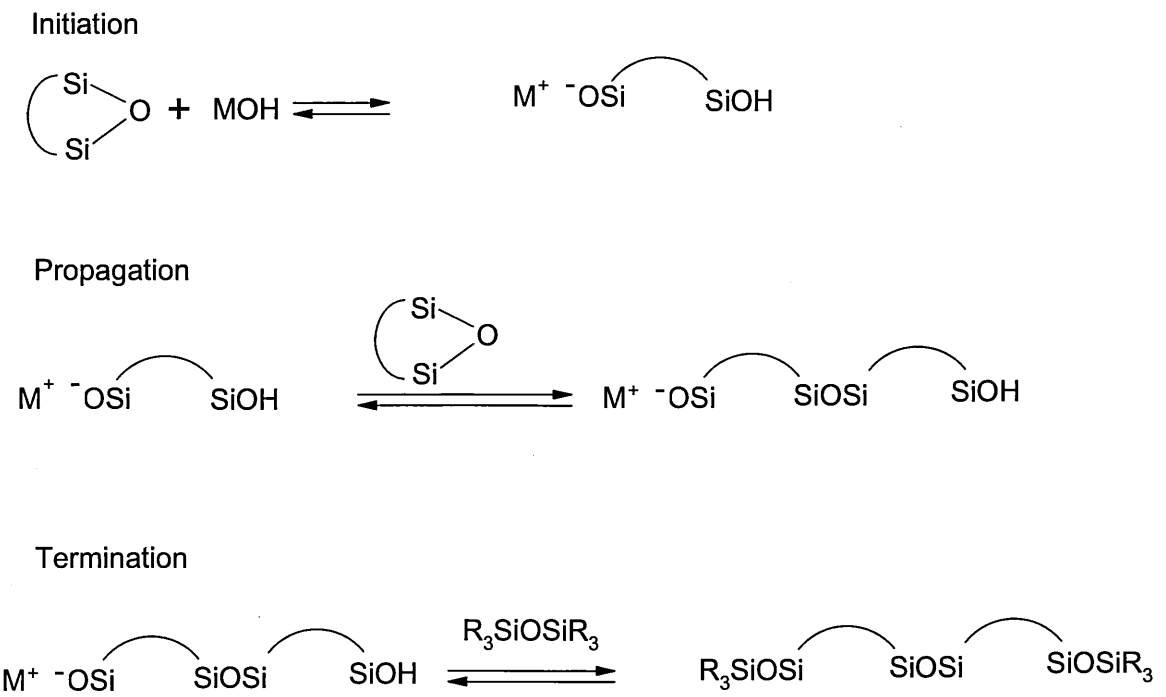


Figure 1.12 Base-catalysed ring-opening polymerisation

This living polymerisation results in a narrow MW distribution and is a particularly attractive route to controlled block copolymers. Unlike most anionic polymerisations, the cyclosiloxane polymerisations are not driven by enthalpy changes. Chain mobility of a typical growing polymer decreases as the polymer MW increases, causing entropy to decrease. Thus, the enthalpy changes must be negative enough to maintain a negative Gibbs free energy ($\Delta G = \Delta H - T\Delta S$) to continue spontaneous polymerisation. In most anionic polymerisations the formation of new bonds (chain growth) results in a larger decrease in enthalpy, and spontaneous polymerisation occurs. In siloxane polymerisation, the energy required to add a monomer into the chain is similar to that of the bond energy in the monomer (D_x). Thus, the overall enthalpy changes are minimal. However, opening the ring of the cyclosiloxane increases the entropy. The degrees of freedom of the siloxane increase upon opening, but as the chain increases in size, entropy decreases (chain mobility/entanglement). Thus, the initial increase in entropy causes the polymerisation to proceed, but as the polymer MW increases, the rate slows.

Both the initiation step and the propagation reaction proceed via a nucleophilic attack on the cyclic oligomer, similar to anionic polymerisation of epoxides.[47] Kantor was the first to corroborate Hyde's suggestion that propagation occurs by attack of a silanolate on a ring (Figure 1.12).[23] The silanolate produced in the initiation step can attack another cyclic, and thus propagation occurs. Grubb and Osthoff confirmed the catalytic species as the metal silanolate by obtaining equal rates of reaction from potassium hydroxide and potassium silanolate catalysed polymerisation of D_4.[48] This was the first kinetic study on anionic polymerisation of D_4 resulting in a first-order dependence on D_4, by measuring vapour pressure changes, and the dependence on potassium hydroxide as half-order. This half-order in catalyst reflects the existence of dormant and active catalytic species and can be viewed as the average multiplicity of the aggregates (metal silanolate living ends).[49]

These kinetics have been confirmed by Chojnowski, who also observed an extensive induction period, which is more pronounced at lower temperatures, before exhibiting first-order kinetics.[50] Many researchers have revealed numerous factors (solvation, polarity of solvents, temperature, catalyst type, and concentration) that affect the kinetics of anionic polymerisation. Unlike typical organic polymers, high MW siloxane polymer is hard to obtain except by increasing the reactivity of the nucleophile (e.g. potassium hydroxide). The rate is affected by various types of ion association. The larger size of the counterion results in a larger separation from the nucleophile and is less likely to aggregate. This weaker ion aggregation becomes even weaker when polar solvents are used.[51] Thus, larger counterions and more polar solvents increase the rate of polymerisation.

Ion-to-ion association, as observed with the silanolate's tendency to form aggregates, greatly impacts the kinetics of polymerisation, as well as the MW distribution.[52, 53] As first discovered by Hyde, polar solvents increase the rate of

polymerisation because the solvent prevents the aggregation of silanolates.[21] Other additives that can aid the dissociation of the ions will also increase the rate of polymerisation.

Originally, the anionic polymerisation of cyclosiloxanes was thought to proceed through free ionic intermediates.[54, 55] However, the conductivity of the solution containing silanolates in polar solvents is minimal.[56] No conductivity has been measured when the polymerisation is carried out in bulk. Ion pairs or aggregates are now considered to be the reactive intermediates.[28, 44] Mazurek and Chojnowski proposed that potassium silanolate forms a crown ether type of ion pair.[47] They proposed a structure where a K^+ resides in the middle of a cyclosiloxane, coordinating to the oxygen atoms as well as the silanolate linear chain. These must disassociate prior to propagation. These catalysts produce a broader MW distribution that tails toward the lower MWs. This can be attributed to a fraction of the chain ends being in the inactive form (aggregates).[57]

The relative reactivity of D_x in ring-opening polymerisation is $D_8 > D_7 > D_9 > D_3 > D_6 > D_4 > D_5$ with potassium silanolate.[47, 54, 55] This observed cyclosiloxane order of reactivity, especially that of the larger ($D_8 > D_7 > D_9$) rings, would not have been predicted. Counterions have been shown to coordinate more readily with larger rings.[58] This is in agreement with the observed activation energies and entropies, which are consistent with a crown ether type mechanism.[47] This would suggest that a large and negative activation entropy is required, based on the more ordered crown ether structure. Similar structures could be involved in the redistribution observed in these systems. The size of the cation should enhance or suppress this coordination, and thus this remains an active area of research.

1.3.3 Acid-catalysed Polymerisation

Strong protic acids, such as H_2SO_4, CF_3SO_3H, and $HClO_4$ induce polymerisation of cyclosiloxanes.[59] Weaker acids generally do not polymerise cyclosiloxanes, but CF_3CO_2H has been moderately effective.[60] Acidic conditions can be used to produce polymers with base-sensitive groups, such as Si–H or Si–RSH. A major drawback of acid polymerisation is the formation of cyclosiloxanes early in the process, as discussed in Section 1.2.3 Hydrolysis/Condensation. In contrast to anionic polymerisation of cyclosiloxanes, the acid-catalysed ring-opening polymerisation mechanism is less clear. Although both acid- and base-catalysed polymerisations provide similar products, their mechanisms appear to be quite different. D_4 polymerisations catalysed by sulphuric acid and trifluoromethanesulphonic acid (triflic acid) appear to follow a step growth process based on the resulting MW distribution and conversion of D_4.[61, 62] In step growth polymerisation two opened oligomer units condense to form one polymer unit. An opened oligomer unit formed from the initiation step opens a new oligomer unit, and the combined molecule can open another in the propagation step of a living polymerisation.

There is an initial induction period during which the MW increases as MW distribution broadens until it conforms to step growth polymerisation.[61] Various low MW linear and cyclosiloxanes appear early and remain stable throughout the polymerisation.[62] The rate at which oligomers participate in the equilibration reaction in acid-initiated polymerisation of dimethylsiloxanes follows $D_3 > MM > MDM > MD_nM > D_4$, while the order of reactivity towards basic catalysts is $D_3 > D_4 > MD_nM > MDM > MM$.[23, 28] Kantor et al. postulated the siloxane oxygen as the site of initial attack during ring opening, due to its basicity. They proposed that protonation of this oxygen leads to the intermediate, with the lone pair of electrons on the siloxane oxygen acting as the electron donor. This differs from base polymerisation, in that the base itself acts as the electron

donor. Alkyl groups on silicon donate electron density. This increases the basicity of the lone pair of electrons on neighbouring oxygens. Thus, M units react more rapidly under acidic conditions. Conversely, a base (nucleophile) attacks silicon in T units because the T silicon can more easily expand its coordination sphere.[4] In acid-catalysed polymerisation the M units participate in the reaction competitively with the D units, causing a competition between small molecules and polymers. Reduction in the rate of acid polymerisation of cyclosiloxanes is observed with electron-withdrawing R groups on the silicon. If one of the eight methyl groups in D_4 is replaced with an R group, the rate decreases according to Me > CH_2Cl > Ph > C_6H_4Cl.[63] Acid-catalysed ring-opening polymerisation conditions can cause cleavage of phenyl and vinyl groups, resulting in branching as well as by-product benzene. In acid-catalysed polymerisation of D_4, the MM end-capping units participate in the reaction competitively with the D units, as mentioned earlier (curve A in Figure 1.13).[28] Base-catalysed polymerisation of D_4 initially produces a rapid increase in MW as D units are added, followed by a decrease in viscosity to an equilibrium MW distribution as the MM units participate in the reaction later (curve B in Figure 1.13).[28]

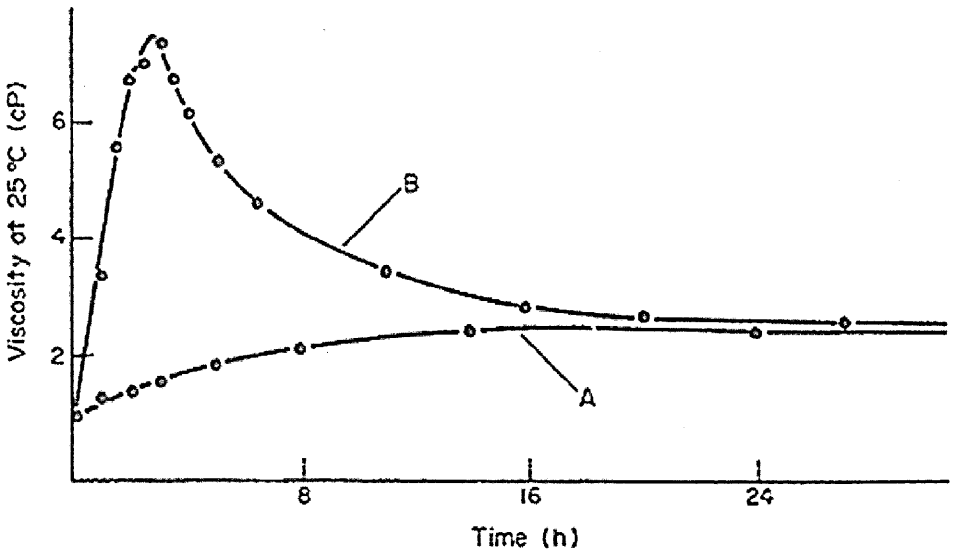


Figure 1.13 Viscosity versus time for 1 mol MM and 1 mol D_4; curve A 4% H_2SO_4; curve B 0.1% Me_4NOH

*Reprinted from: Kendrick, T. C.; White, J. W.; Parbhoo, B., Polymerization of Cyclosiloxanes. In Comprehensive Polymer Science, G. C. Eastmond, A. L., S. Russo, P. Sigwalt, Ed.; Pergamon Press: **1989**; Vol. 4, pp 459-523, with permission.*

Wilczek et al. measured the initial rate of polymerisation of D_4 with triflic acid as:[64]

$$k_p = [CF_3SO_3H]^{2.2}\,[D_4]^{0.7}$$

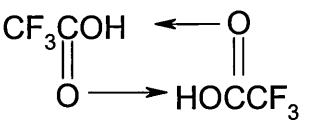
Higher conversions show first-order dependence on D_4, and an order in catalyst of 2.7 with both D_4 and D_6 starting material, as shown by Sigwalt, et al..[62] An induction period has been observed at low catalyst (1 mmol l^{-1}) concentrations. D_3 polymerisation shows a similar order in triflic acid and a negative order in trimer. Wilczek and Chojnowski studied the kinetics of trifluoroacetic acid-catalysed ring opening of D_3/D_4 in dichloromethane (CH_2Cl_2) and *n*-heptane, and proposed that three processes play a role in the mechanism.[60]

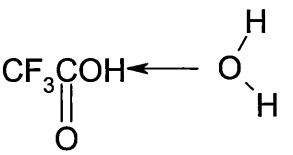
$$HA + SiOSi \rightleftharpoons SiA + HOSi \quad (1)\ \text{acidolysis}$$

$$SiOH + SiOH \rightleftharpoons SiOSi + H_2O \quad (2)\ \text{condensation}$$

$$SiA + H_2O \rightleftharpoons SiOH + HA \quad (3)\ \text{hydrolysis}$$

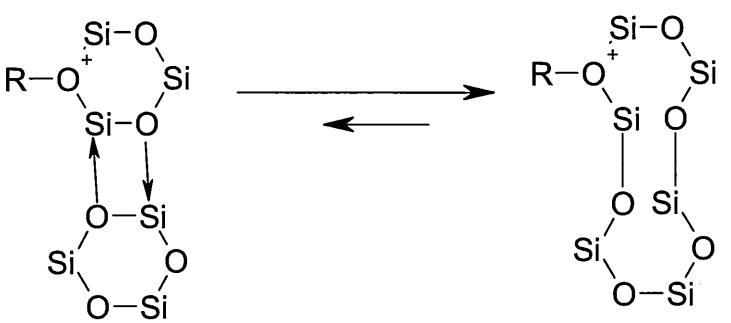
HA represents the acid, where A = CF_3COO in this case. The authors determined that the addition of water strongly increases ester formation, (1). They also showed that the acid exists predominately as a hydrogen-bonded cyclic dimer, but only as a linear complex with water.





These H-bonded complexes are weaker in dichloromethane than in the heptane solvent (competitive interaction of acid with the more polar dichloromethane). The authors suggest that the formation of H-bonded complexes, such as acid-acid as discussed above, and the competition between H-bonded complexes and acid-monomer complexes are the reasons for some of the kinetic results, i.e., multiple and partial orders. Wilczek and Chojnowski suggest the stronger ion (triflate) favours onium ion active centre formation. Weaker acids (for example, CF_3COOH) have acid-acid interactions and other H-bonded species (acid-substrate) that are involved in the mechanism leading to complex (non-integer) orders in acid. The strong triflate-substrate interactions diminish the acid-acid interactions. Wilczek and Chojnowski used infrared spectroscopy (IR) (–OH in COOH appears at 3500 cm^{-1}) to determine acid-substrate kinetics.[65] They chose MM as the substrate to avoid the complications of polymerisation. When trifluoroacetic acid and MM are combined, the concentration of free acid drops while acid-substrate complexes are formed. This supports the formation of an acid-MM H-bonded complex. The initial decrease in acid concentration is also observed in acid-catalysed cyclosiloxane polymerisation. Then the acid concentration increases as condensation releases acid and water during polymerization. D_3 and D_4 are thought to polymerise by similar mechanisms, but D_3 polymerises more rapidly. Wilczek and Chojnowski believe this is due to hydrogen

bonding, which is easier with the more basic D_3. The lone pair of electrons on the oxygen in D_x are slightly basic, as is shown by their ability to be protonated. The ring strain in D_3 was thought to cause the back donation of electrons from the oxygen to the silicon ($p_\pi - d_\pi$) to be less effective than in the strain-free D_4, or more recently, based on ab initio calculations, the electrons participate less in the covalent bonding region of D_3. This allows the electrons on oxygen in D_3 to be more available for interactions with acid. The higher rate of D_3 polymerisation was generally believed to be related to ring strain, recently ring strain is hypothesised to allow more H-bonding complexes. Triflic acid-polymerised D_3 produces cyclics in the series D_{3x} (D_6, D_9, etc.) before reaching equilibrium. Chojnowski et al. explain this phenomenon by examining the competition between intra- and intermolecular reactions. New chain ends form cyclics initially, but as the polymerisation progresses, the chain ends are too far from their origin for ring closure to be probable.[60] Sigwalt disagrees with this explanation and offers a ring-expansion mechanism which occurs by attack on the oxonium sites of the D_3^+ species:[66]



Wilczek and Chojnowski showed the cocatalytic effect of adding water on the rate of polymerisation of D_3 in 1979.[67] Chojnowski postulates the reason for this to be hydrolysis of the triflate ester, as well as hydration of acid-monomer complex (H-bonding). Sigwalt et al. showed a reduction in the rate of polymerisation with the addition of water to a triflic acid-catalysed system.[62] They concluded that water accelerates the

polymerisation of D_3 only at low triflic acid concentrations.[44] Sigwalt et al. also showed that water inhibits the rate of D_4 polymerisation at both low and higher water concentrations. Thus the hydrolysis of triflic acid cannot explain the differences in D_3 and D_4 polymerisation, which is contrary to Chojnowski's theory.

A mechanism, can be proposed that is consistent with the observations made thus far. The mechanism is separated into four parts: initiation; step growth, chain growth, and termination, as first suggested by Wilczek and Chojnowski.[67] Sigwalt has refined this mechanism, and a form of it is detailed in Figure 1.14.[66, 68]

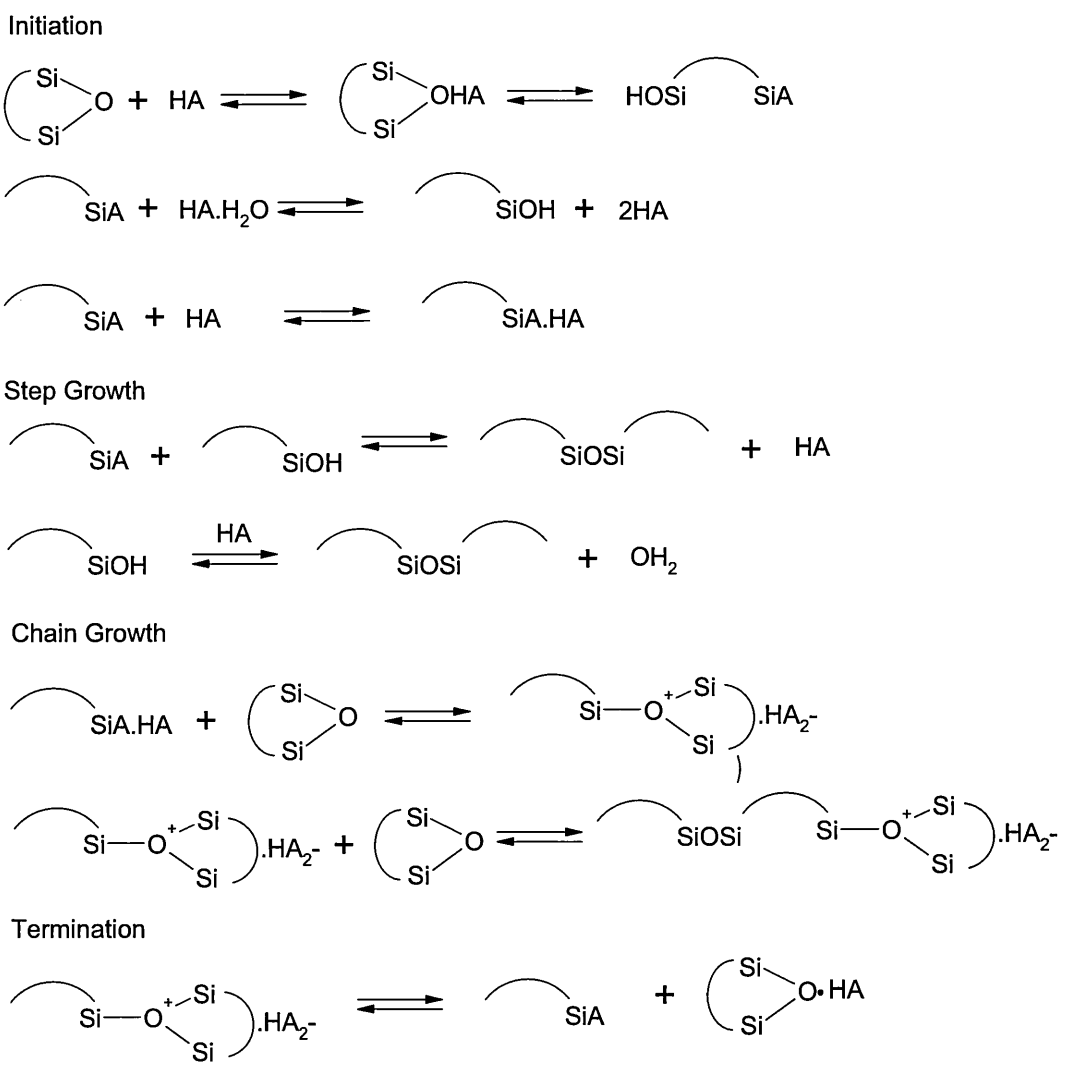


Figure 1.14 Proposed mechanism for triflic acid-catalysed ring-opening polymerisation

This mechanism could explain the negative first-order in $[D_3]_0$, but not the higher negative orders observed by some researchers. Also, this mechanism could account for a second-order reaction with respect to triflic acid, but not the higher orders that have been reported. Formation of rings in the series D_{3x} can be explained by the intramolecular step growth reactions or the second chain growth reaction involving chain expansion. The second initiation reaction is used to explain the rate reduction effect of water. Unfortunately, the rate acceleration effect of water has yet to be satisfactorily explained.[60, 66, 67] A proposal by Sigwalt suggests small amounts of water may disrupt the D_4-acid complex, and large amounts of water may form a more active hydrated acid. The reaction scheme in Figure 1.14 cannot account for all the reported details and is already quite complex. Thus, considerably more research is needed in the mechanistic area of acid-catalysed polymerisation of cyclosiloxanes. Most of the recent work has not included the once-proposed silicenium ion in the mechanism.[45]

Brönsted acids (proton donor) discussed thus far catalyse polymerisation via protonation of the siloxane oxygen, as do water-complexed Lewis acids, which generally generate their protons from water. Lewis defined an acid as an electron pair acceptor and a base as an electron pair donor. Lewis acids are thought to catalyse in the same manner as Brönsted acids. Thus in siloxanes, the oxygen would be expected to share its lone pair of electrons with the catalyst, a proton with Brönsted acids, or a metal centre of Lewis acids such as Fe in $FeCl_3$. However, Kendrick has shown that neither anhydrous ferric chloride nor anhydrous HCl catalyse the polymerisation of D_4 (octamethylcyclotetrasiloxane).[69] When the two acid catalysts are combined, the reaction proceeds, but the catalyst resembles a protic acid, $H^+[FeCl_4HFeCl_4]^-$. This implies that a proton, which can be gained by hydrolysis with water, is necessary for polymerisation.

Thus, the protonated Lewis acid has been transformed into a Brönsted acid. Some very strong Lewis acids (such as ethylboron sesquitriflate (EBST)) have been shown to produce oligomeric siloxanes, and even higher MW polymers, but at a slower rate than an equivalent amount of Brönsted acid.[70] Polymerisation of 1.7 M D_3 with 3.8 x 10^{-4} M EBST in CH_2Cl_2 resulted in minimal yield of oligomers and no polymer (methanol insoluble polymer) after 5 days at 25°C.[70] However, 1.1 M D_3 with 4.8 x 10^{-4} M triflic acid in CH_2Cl_2 produced 63% polymer in 30 minutes at 25°C. The rate of polymerisation increases further when the polarity of the solvent increases.

Jordan treated 1.7 M D_3 with 2.5 x 10^{-4} M EBST in a 84/16 volume mixture of CH_2Cl_2 /CH_3CN to produce 63% polymer in 18 hours at 25°C.[70] This was very different from the minimal reaction observed in pure CH_2Cl_2, as described above. Unfortunately, the process used to dry the acetonitrile may have not removed all of the moisture, as acetonitrile is difficult to dry, and thus protons needed to be rigorously excluded by the addition of a hindered pyridine, DBMP (2,6-di-*tert*-butyl-4-methylpyridine). Brown and Kanner first reported the use of hindered pyridines to differentiate between protic and Lewis acids.[71] "Proton sponges" of the hindered amine and pyridine type display an unusual basicity but poor nucleophilicity due to the steric hindrance around the amino groups.[72] Hindered pyridines are nonnucleophilic bases but are capable of stopping reactions initiated by protonation.[73] Normal pyridines do react with Lewis acids. Interestingly, when Jordan treated 0.9 M D_3 with 2.3 x 10^{-4} M EBST along with 2.5 x 10^{-4} M DBMP in a 76/24 volume mixture of CH_2Cl_2/CH_3CN, no polymer was formed even after 10 days at 25°C. Addition of more EBST catalyst or water induced polymerisation. The fact that the addition of water induces polymerisation is explained by the hydrolysis of the EBST catalyst to form triflic acid, a protic acid. Jordan and co-workers dismiss an interaction between the catalyst and the proton sponge based on

Gandini's work, where it was shown that Lewis acids do not react with hindered pyridines.[73]

Gandini et al. reported that the addition of the proton sponge DBMP did not affect the rate of aluminium triflate-catalysed polymerisation of isobutene.[74] Gandini and Marti'nez then claim DBMP decreases the rate of Lewis acid ($TiCl_4$, $SnCl_4$, and $EtAlCl_2$) catalysed polymerisation of isobutene and α-methylstyrene in various solvents.[73] After a critical concentration of DBMP had been added, the polymerisation rate was not reduced further, so they claim the reduction was due to residual moisture. They also state that commercially available sterically hindered amines contain impurities, such as monosubstituted pyridines, which can provide misleading results. In order to dismiss DBMP interaction with the Lewis acid, Gandini et al. used ^1H nuclear magnetic resonance (NMR) to show an interaction between the Lewis acid and water, and more importantly, used this technique to show a lack of interaction between the free Lewis acid and DBMP or $HDBMP^+$.[73] Gandini addresses Sigwalt's 1983 claim of an aluminium chloride DBMP complex only as "peculiar" and deserving of "further attention".

Bennevault et al. showed that sterically hindered amines (DBMP and DBP(2,6-di-*tert*-butylpyridine)) inhibit the polymerisation of chloroethyl vinyl ethers with $ZnCl_2$.[75] The authors speculate that a complex between $ZnCl_2$ and DBP is the cause of the reduction in polymerisation. An ultraviolet (UV) absorption spectroscopy shift from 260 nm with DBP in $CHCl_3$ to 270 nm with 1:3 DBP:$ZnCl_2$ in $CHCl_3$ was observed, suggesting an interaction between the amine and the Lewis acid salt. No shift in the UV absorption was observed with benzene and $ZnCl_2$, suggesting that the $ZnCl_2$ interacts with the nitrogen of the hindered pyridines. Bennevault et al. modelled the $ZnCl_2$-DBP complex, which resulted in a 1.94 Å distance between the nitrogen and zinc atoms. Sigwalt et al. reported a calculated nitrogen-to-aluminium bond distance ≅ 2Å in an $AlCl_3$-DBMP distorted

tetrahedron model.[76] The authors compare this distance to the 1.847 Å observed by X-ray in the structure of CH_3CH_2COCl-$AlCl_3$. They used ^1H NMR to observe a strong complexation between DBMP and $AlCl_3$ in $CDCl_3$. Where the aromatic H in DBMP was 6.95 ppm, the protonated DBMP was 7.65 ppm, and the complex was 7.56 ppm. Similar shifts were given for *p*-CH_3 and the *tert*-butyl. Interestingly, no interaction was observed in the ^1H NMR for a DBMP-$TiCl_4$ complex. The authors attempt to explain this in terms of the bulkier and symmetrical tetrahedron around the Ti and a weaker acidity, but conclude with the comment "the effects of sterically hindered pyridines in cationic polymerisation are not as simple as indicated by previous investigators".[76]

Recently, some water-tolerant Lewis acids have been used in organic synthesis. Kobayashi used some of the lanthanide series of triflates for aldol, Michael, allylation, Diels-Alder, and Friedel-Crafts reactions.[77] Kobayashi also identified some Lewis acids with perchlorate or triflate ligands that are stable in water, although many are weakly catalytic.[78] Lewis acids of Fe (II), Cu(II), Zn(II), Cd(II), Pb(II), Sc(III), Y(III), and Ln(III) were stable in water and active to an aldol reaction. Metal compounds with pK_h values of 4.3 to 10.08 and water exchange rate constants (WERC) greater than $3.2 \times 10^6\ M^{-1}s^{-1}$ gave more than 50% yields. The author concludes that when pK_h values are less than 4.3 they easily hydrolyse and oxonium ions are formed. When pK_h values are higher than 10.08 the cations are too stable. A small $(electron)^2$/(ionic radii) equals a fast WERC.

In recent work, Olah et al. showed that polymerisation of cyclosiloxanes can be propagated through long-lived ternary silyloxonium ions.[79] The initiator was produced by reacting tetrakis (pentafluorophenyl)borate (TPFPB) with a silane (e.g. Me_3SiH). Good yields (70 to 90%) of polymer were only obtained when the monomer-to-initiator ratio was higher than 50, while the monomer concentration ranged from 1 to 2 M. These conditions resulted in a dispersity of 1.8 to 2.5. When the monomer-to-initiator ratio was

too low, the authors report abstraction of the halide along with other side reactions giving complex results. The attachment of bulky ligands to Lewis acids often leads to more reactive acids because the formation of deactivated complexes of associated Lewis acids is hindered.

1.4 Isomeric Interconversion

Lewis acids have been shown to catalyse the isomerisation of cyclosiloxanes. In 1978 Frye and Spielvogel reported the interconversion of 2,6-*trans*-diphenylhexamethylcyclotetrasiloxane (2,6-*trans*) to an equimolar mixture of the *cis* and *trans* isomers of the cyclosiloxane.[80] They reported that the interconversion occurred rapidly in the presence of a Lewis acid and a polar aprotic solvent (nitroalkanes). They reported little or no 2,4-isomers were produced, nor were any linear oligomers or other cyclics observed (Figure 1.15).

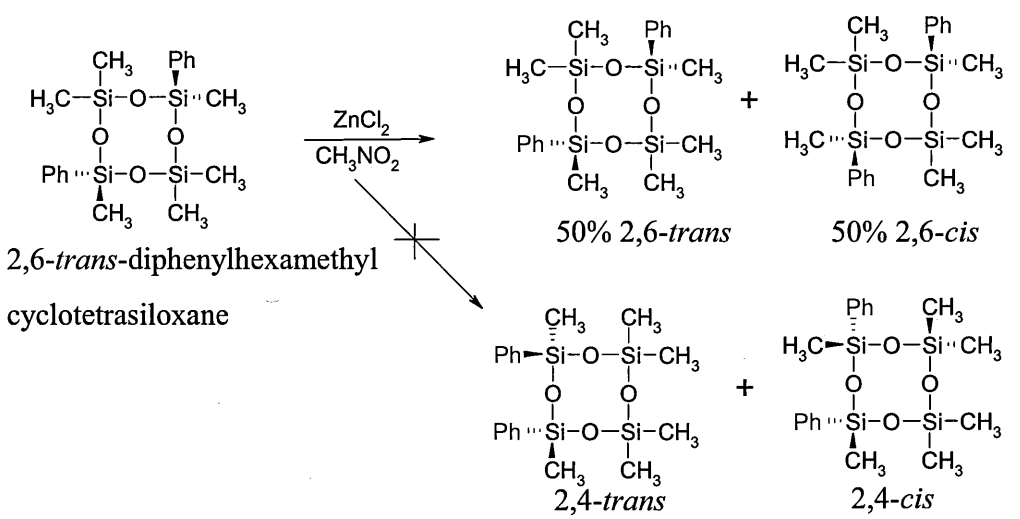


Figure 1.15 Isomer interconversion of 2,6-diphenylhexamethylcyclotetrasiloxane

The same 50:50 mixture of isomers was found when they started with the 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane isomer. The interconversion appears to be highly

selective and was the basis for a patent in 1975.[81] The authors demonstrated conditions where this reaction was efficient enough to produce 2,6-isomers containing less than 0.2% of the 2,4-isomers. Frye and Spielvogel performed the experiments by heating the siloxane in solvent with catalyst in a closed container. A 90°C reaction containing 4.2 g nitromethane (solvent) and 4.2 g of 2,6-*trans*, with the amounts of $ZnCl_2$ shown in Table 1.1, was analysed by GLC.

$ZnCl_2$ %, based on weight of siloxane	GLC results after 64 h		GLC results after 82 h	
	% 2,6-*cis*	% 2,6-*trans*	% 2,6-*cis*	% 2,6-*trans*
10	54	46	52	48
1	12	88	15	85
5	51	49		

Table 1.1. Spielvogel and Frye data from 90°C reaction of 2,6-*trans*-diphenylhexamethylcyclotetrasiloxane in nitromethane with zinc chloride catalyst[80]

The GLC did not show peaks for the 2,4-isomers, but only interconversion producing nearly a 1/1 mixture of the 2,6-isomers. The authors showed this interconversion reaction proceeded to an equilibrium mixture (25% *cis*, 75% *trans*) of the trimer isomers with 5% $ZnCl_2$ without additional heat, at room temperature, with either *cis* or *trans* $(PhMeSiO)_3$ ($^{Ph}D_3$). This enhanced reactivity over the D_4 cyclic could be explained by the ring strain of the D_3. The only other cyclic the authors mention is a trifluoropropyl methyl D_3 as an example in the patent.[81] A mixture of 0.49 g of *trans*-tris(3,3,3-trifluoropropyl)-trimethylcyclotrisiloxane, 1.42 g of 2-nitropropane, and 0.0282 g of anhydrous $ZnCl_2$ was stirred for 18 h at 25°C. Water, equal to the total volume of the mixture, was added to dissolve the $ZnCl_2$. The nitropropane was devolatilized at 25°C under 1 to 2 mm pressure. ^{19}F NMR was used to analyse the residue and depicted a 0.09/0.91 *cis*/*trans* ratio. This is the only example the authors give where water was added to the reaction mixture. All other examples are either stated as anhydrous, or nothing

concerning water was mentioned. Also, the final *cis/trans* ratio is not representative of the predicted D_3 equilibrium isomeric mixture.

Frye and Spielvogel proposed two possible mechanisms to explain their observations. Both mechanisms involve breaking of a Si–O bond and thus the rapid opening and reformation of the cyclic molecule.[80] It may be important to note that no data were offered in support of these proposed schemes, nor has anyone, subsequent to this work, offered additional insight into this interesting observation. The authors proposed the siloxane bond to break by attack of the acid, as shown in Figure 1.16.

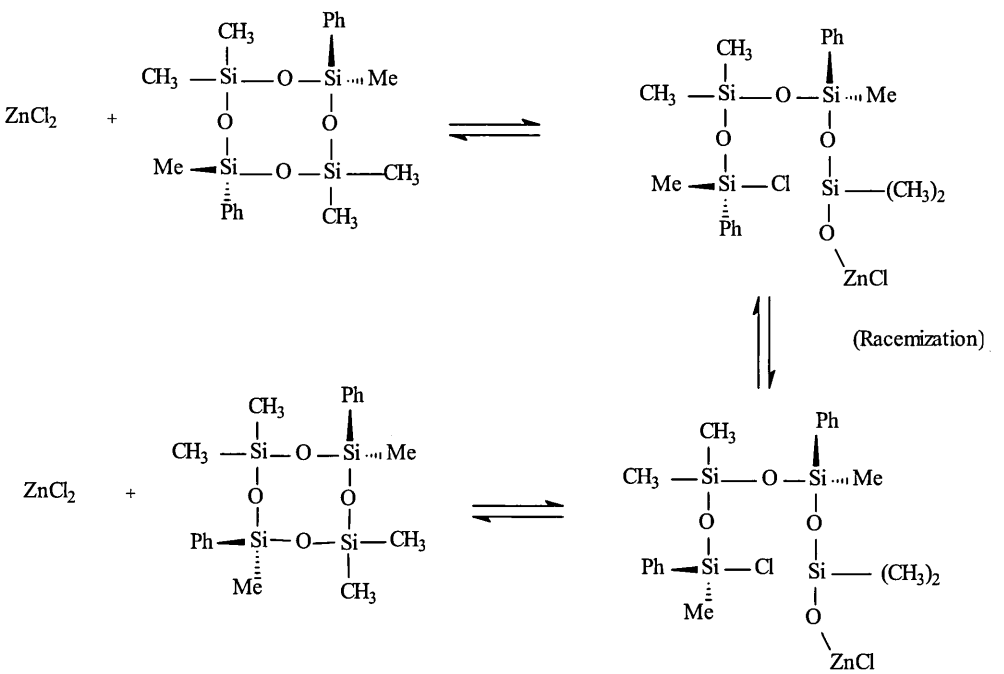


Figure 1.16 2,6-Diphenylhexamethylcyclotetrasiloxane isomer interconversion ring-opening mechanism #1 proposed by Frye and Spielvogel

The opened siloxane ring structure proposed in Figure 1.16 must then convert from one stereoisomer to the other, followed by closure to regenerate the ring in the same position. This must happen without any other siloxane bonds breaking and/or reforming because that would lead to other isomers, i.e. 2,4-isomers and/or linear species. Also, simple rotation of the tetrahedral silicon about the Si–O bond of the ring-opened structure

does not effect a change from a *trans* to a *cis* isomer.

Frye and Spielvogel offered a second mechanism, which also involves a ring-opened species. Figure 1.16 shows their second proposed mechanism, which involves a siliconium ion. A siliconium ion is a silicon atom with only three bonds and is thus cationic.

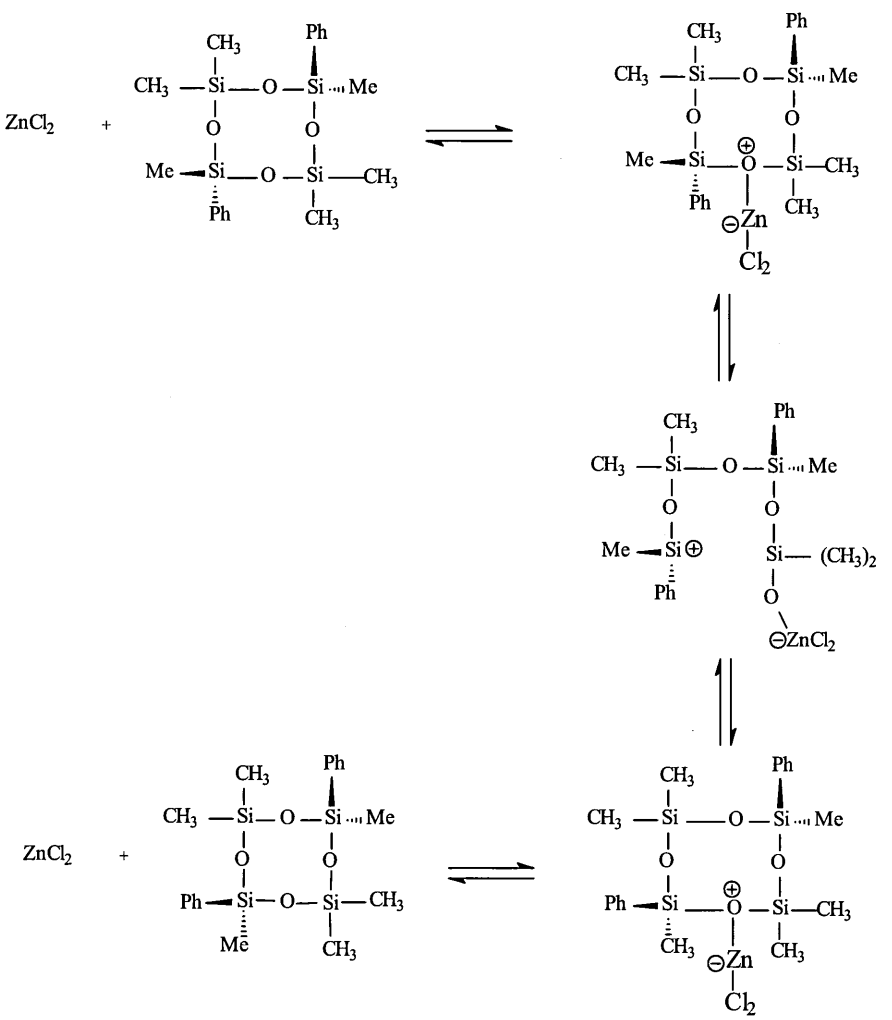


Figure 1.17 2,6-Diphenylhexamethylcyclotetrasiloxane isomer interconversion ring-opening mechanism #2 proposed by Frye and Spielvogel

The Lewis acids $CaCl_2$ and $HgCl_2$ were not effective for this interconversion in 2-nitropropane, while $AlCl_3$ was moderately active. The most efficient catalyst attempted by Frye and Spielvogel was $FeCl_3$; 0.5% catalyst provided complete interconversion in 2

hours at 25°C in 2-nitropropane. They also briefly mentioned small amounts of H_2SO_4 (100 ppm with respect to the siloxane) yielding interconversion, but a larger amount, 4%, of the 2,4-isomers was observed as well. The authors protected the metal halides from moisture, but detailed procedures were not given.

None of the other solvents the authors used were as efficient as the nitroalkanes. In fact, the only other solvents mentioned as effective for the interconversion were aryl phosphates, which required higher temperatures (220°C with $ZnCl_2$, and 60°C with $FeCl_3$). Acetonitrile, ketone, and glymes (glycol diethers) proved ineffective under these conditions.

Finally, when dimethylformamide was used as the solvent other by-products were formed, possibly the result of redistribution. Frye and Spielvogel showed that more dilute solutions increased the reaction rate. For example, a reaction containing 4.2 g nitrobenzene solvent and 4.2 g of 2,6-*trans*, with 0.21 g of anhydrous $ZnCl_2$ catalyst, produced 46.8% 2,6-*cis* in 2.8 days at 90°C (34.4% after 24 h). However, when 75% nitrobenzene, based on the weight of siloxane, was used, 47.8% 2,6-*cis* was obtained in 20 h.[81] The authors used reagent-grade solvents, with the addition of molecular sieves to maintain their dryness.

Chang et al. recently showed the interconversion of 2,4,6-*cis*-trimethyl-2,4,6-triphenylcyclotresiloxane to the expected equilibrium *cis* to *trans* isomeric mixture.[82] The reactions were carried out in DMSO (as well as CD_3CN, but at a slower rate) and catalysed by n-$C_8H_{17}NH_3BF_4$. Polymerisation of the 2,4,6-*cis* isomer was observed with 0.1 M $LiBF_4$. Interconversion was observed at a slower rate when 0.08 M LiCl was used as the catalyst. This is not easy to understand, as the Cl^- is the stronger nucleophile and would be expected to lead to ring-opening polymerisation. The liberation of F^- from the BF_4 seems plausible and could be the source of nucleophiles in their $LiBF_4$ catalysed

reactions. The authors suggest a pre-complex formation of the catalyst with the cyclosiloxane, where the cation coordinates with the oxygen which allows for nucleophilic attack on the adjacent silicon. They suggest both the $R_nNH_{4-n}^+$ and BF_4^- are necessary for interconversion. The formed pentacoordinate silicon intermediate can then undergo Berry pseudorotations as discussed in Section 1.5. The proposed mechanism does not involve silicon-oxygen bond breaking. A representation of the mechanism discussed is shown in Figure 1.18.

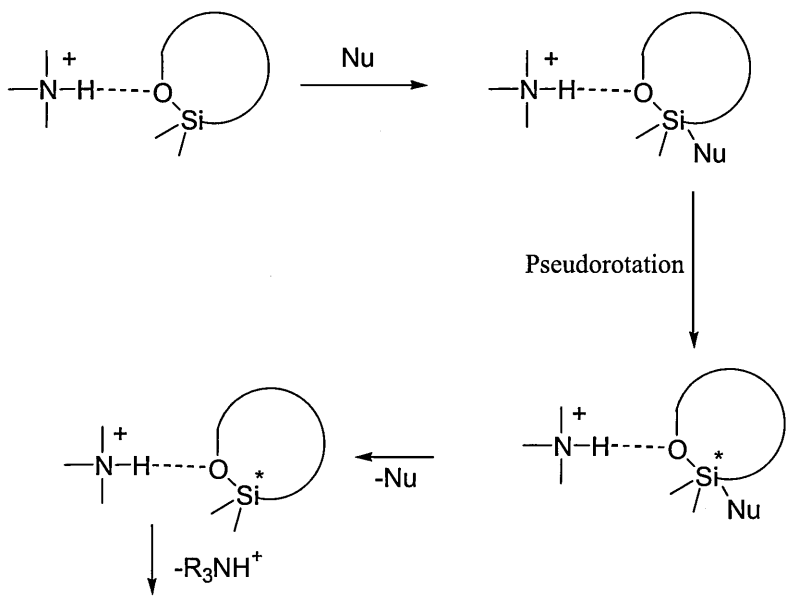


Figure 1.18 Chang et. al. mechanism for $R_nNH_{4-n}BF_4$ catalysed interconversion of 2,4,6-*cis*-trimethyl-2,4,6-triphenylcyclotrisiloxane in DMSO

The order in catalyst (determined from a plot of ln (k^{cat}) versus ln [$R_nNH_{4-n}BF_4$]) was determined to be 2.2 $\pm$ 0.2 for the ammonium salts studied.

In order to further understand the interconversion reaction and the mechanistic pathway, a study of the contributing factors is necessary. The polarity of the solvent plays an important role as Frye and Spielvogel showed with polymerisation versus interconversion results. The ability of the solvent to supply protons and act as a nucleophile will be shown to produce different products in this reaction; as well as

concentration and type of catalyst and impact of temperature. A more detailed mechanism can be proposed once these factors and the number of molecules that participate in the rate-determining step are known, i.e. order in substrate, catalyst, etc. A kinetic analysis of the interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane (2,6-*cis*) with Brönsted acids (Chapter 2) and Lewis acids (Chapter 3) was undertaken. Section 1.4.1 Kinetic Analysis that follows gives the background on kinetics for Chapter 2 and Chapter 3.

1.4.1 Kinetic Analysis

The rate of a reaction is defined as the change in concentration of the reactants per unit time. This can be followed by observing the disappearance of a reactant (2,6-*cis* in our case) or the appearance of a product (2,6-*trans*). Assuming the reaction is first-order, the rate is dependent on one factor only, the reactant concentration, raised to the first power:

$$\text{Rate of reaction} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

where [A] is the concentration of our reactant (2,6-*cis* in our case), t is time, and k is the rate constant. Integrating this equation results in:

$$[\text{A}]_t = [\text{A}]_0 e^{-kt}$$

Where $[\text{A}]_t$ is the concentration of A at time t, and $[\text{A}]_0$ is the initial concentration of A. This equation represents the exponential curve of the data produced in Figure 2.2. Taking the natural log of each side gives:

$$\ln[\text{A}]_t = \ln[\text{A}]_0 - kt$$

which represents a line, with a slope of $-k$, and a y-intercept of $\ln[\text{A}]_0$. Thus, if a reaction obeys first-order kinetics, the plot of log of concentration of the reactant against time will

produce a straight line. The slope of this line is the rate constant, k. In the proceeding interconversion reactions, the concentration at time t of the starting material minus the equilibrium concentration (2,6-cis_t–2,6-cis_{eq}) must be analysed, since the reaction achieves equilibrium with approximately 50% of the starting material remaining.

The production of 2,6-*trans* isomer and the loss of 2,6-*cis* isomer from one reaction are plotted versus time to obtain the rate of the reaction. The slope of these lines produces the rate of the reaction, and the two slopes should be equivalent, assuming no other isomers/linears are formed, and our internal standard factor is accurate. The rate of a reaction is proportional to the concentration of the reactants, and as the reaction proceeds, the rate will decrease. We know the initial concentration of the reactant, so calculating the rate should be straightforward. Only the linear portions of the data are used for determining the kinetic rate of the reaction. This is typically the data representing up to the first 80% of the reaction. In this case, we are following the loss of 2,6-*cis* isomer, and the production of 2,6-*trans*.

1.4.1.1 Second-order Kinetics

If a reaction is second-order, the rate is dependent upon the concentration of two reactants or that of a single reactant squared. We will only consider the case of a single reactant since our system only contains one reactant. The solvent (present in large excess) and the catalyst (typical small catalytic quantities) are not being considered as reactants. As such, the rate is dependent on one factor raised to the second power.

$$\text{Rate of reaction} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$$

Integrating this equation results in:

$$\frac{1}{[\text{A}]_t} = \frac{1}{[\text{A}]_0} + kt$$

which represents a line, with a slope of k, and a y-intercept of $1/[A]_0$. Thus, if a reaction obeys second-order kinetics, the plot of the inverse of the concentration of the reactant against time will produce a straight line. The slope of this line is the rate constant, k.

1.4.1.2 Activation Energy

The rate equation discussed earlier accounts for the impact the reactants concentration has on the rate, but explicitly ignores other factors, incorporating them into the rate constant k. The Arrhenius equation includes the temperature effects on k as a means to elucidate the activation energy of a reaction, as follows:

$$k = A\mathrm{e}^{-E_a/RT}$$

where A is the Arrhenius constant or the pre-exponential factor, E_a is the activation energy of the reaction, R is the gas constant (8.314 J/mol K), and T is temperature in units Kelvin. The activation energy, E_a, is the difference between the energy of the reactants and the transition state, which lies between the reactants and products. In other words, the activation energy is the minimum energy that reactants must have in order to form products. The Arrhenius constant, A, is related to the frequency of collisions, depends mostly on orientation factors, and varies slightly with temperature. A small Arrhenius constant implies a highly oriented reaction. When the natural log of each side of the equation is taken, the following equation results, which represents a line:

$$\ln k = \ln A - \frac{E_a}{RT}$$

The slope of this line is equal to $-E_a/R$ and the intercept is $\ln A$. Thus, the slope from a plot of $\ln k$ at various temperatures against $1/T$ will provide the activation energy, E_a (where E_a = slope x R). The intercept will provide the Arrhenius constant, where the intercept is $\ln A$.

1.4.1.3 Entropy and Enthalpy

H. Eyring introduced another equation used to express the temperature dependence of a rate constant:

$$k = K\frac{k_B T}{h}e^{\Delta S/R}e^{-\Delta H/RT}$$

where k_B is Boltzmann's constant (1.38 x 10^{-23} J/K); h is Planck's constant (6.626 x 10^{-34} J s); R is the gas constant (8.314 J/mol K); T is temperature; ΔS is the standard entropy of activation; ΔH is the standard enthalpy of activation, and K is the transmission factor from transition state theory.[83] For almost all reactions in solution $K = 1$, and thus it is not factored into the equation. After taking the logarithm, the above equation becomes:

$$\ln\frac{k}{T} = \ln\frac{k_B}{h} + \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

A plot of ln (k/T) will be a linear function of $1/T$. The slope of this line will equal $\Delta H/R$, thus ΔH = –slope x R. The intercept = ln (k_B/h) + $\Delta S/R$. Thus, $\Delta S/R$ = intercept – ln (k_B/h). With ln (k_B/h) = 23.76, the equation rearranges to ΔS = 8.314 x (intercept – 23.76).

As entropy (ΔS), or order, becomes more negative the reaction results in more randomness. A negative entropy, or loss of randomness, suggests a more ordered complex which could be represented in a transition state where a tetracoordinate silicon and a nucleophile form a pentacoordinate silicon.

1.5 Pentacoordinate Si

The observed Si–O bond length is about 1.64 Å, which is much smaller than the sum of the atomic radii, which is 1.83 Å (silicon 1.17 Å and oxygen 0.66 Å). A partial double bond character, (p→d)π conjugation, may explain the difference between the calculated silicon and oxygen bond length and the shorter measured length.[45] The electrons in the 3s and 3p orbitals of the silicon atom form σ-bonds with the p electrons of

the oxygen oriented toward the silicon atom. Additional π interaction of the unshared p electrons of the oxygen atom with the unfilled 3d orbitals of the silicon lead to what is known as pπ→dπ bonding. This may explain some of the differences between silicon and carbon compounds, which do not have d orbitals, and in particular their reactivity. Silicon never uses more than two of its five d orbitals ($3d_{z2}$, $3d_{x2-y2}$) to form σ-bonds, due to orientation.[84] This gives the best overlap with the p orbitals of the oxygen, resulting in extracoordination of the silicon atom. In fact, compounds with five, six, and even seven bonds to silicon have been isolated. Typically extracoordinate (greater than 4) silicon species have been observed with fluorine atoms or oxygen or nitrogen ligands. If electron-accepting ligands are attached to silicon, the electron density decreases and partial double bond character may increase. If electron-donating substituents are attached to the oxygen, the negative charge increases, resulting in a possible reduction in the partial double bond character. In spite of the partial double bond character, nearly free rotation around the siloxane bond is possible because partial pπ→dπ bonding does not restrict rotation about the σ bonds of the Si–O bond, unlike π–π bonds.

The purpose of this discussion is to focus on pentacoordinate silicon species that are involved as intermediates in the reaction mechanism. When $3d_{z2}$ is hybridised with 3s and 3p orbitals, a sp^3d hybrid orbital is formed.[85-91] The normal tetravalent silicon atom, which is a tetrahedron, takes the shape of a trigonal bipyramid in this pentacoordinate silicon hybridised complex (Figure 1.19).

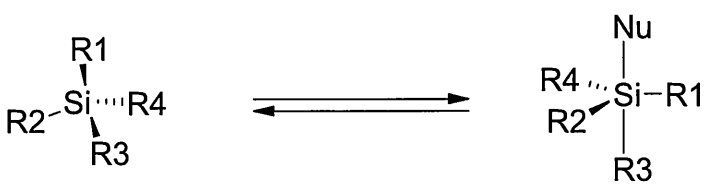


Figure 1.19 A tetracoordinate silicon in tetrahedron form that takes the shape of a trigonal bipyramid in pentacoordinate form (Nu = nucleophile)

The R-Si-R angle in a tetrahedron is 109.5°. The R1-Si-R2 angle in the trigonal bipyramid is 120°, and the R1-Si-Nu angle is 90°. Corriu summarized data from several groups on pentacoordinated silicon species with fluorine.[92] X-ray analysis of these fluorosilicates shows the geometry is close to a trigonal bipyramid with the organic groups in the equatorial positions. Thus, the more electronegative fluorine atoms occupy the axial positions. Also the lengths of the Si–F bonds in the axial position are always longer than those occupying the equatorial positions, and both lengths increase with steric interactions.

Nucleophilic attack of a tetrahedral silicon species forms a pentacoordinate silicon transition state or intermediate. Thus, understanding pentacoordinate silicon species and their reactivity is essential to understanding nucleophilic substitution at silicon and its mechanism. Nucleophilic substitution at silicon can proceed either with retention or inversion of configuration depending on the leaving group, the nucleophile, and the other ligands on silicon. Inversion is observed when the nucleophile attacks opposite the leaving group, while equatorial attack leads to retention of stereochemistry at silicon. The rate of substitution is greatly decreased as the ligands become bulky and steric interactions hinder the reaction. Inversion at Si with this S_N2 mechanism typically occurs with good leaving groups (Cl, Br, I). Retention is observed with leaving groups that have very strong bonds to Si (F, OR) and with leaving groups that are not highly polarised (H, C). Nucleophilic substitution (S_N2) at C in a single-step reaction leads to inversion of stereochemistry. The bonds to the leaving group and the nucleophile are lengthened in the transition state.

Retention of stereochemistry in carbon usually implies a double inversion process (sequential S_N2 reactions).[93] Sommer proposed a mechanism for silicon with an S_N1 dissociation followed by same-side nucleophilic attack, known as S_Ni (substitution nucleophilic internal), with retention of configuration.[4] S_Ni is very rare for carbon

(decomposition of ROCOCl into RCl and CO_2 is an example), but is more viable for silicon because the longer bonds to silicon leave room for the same-side approach of the nucleophile. Also, the low-lying orbitals on silicon form a stable extracoordinate species. S_Ni is proposed to occur through equatorial attack of the nucleophile, but is suggested to proceed more likely through a 4-centred intermediate involving assistance from the counterion of the nucleophile. Thus, solvation of this counterion should decrease retention according to the S_Ni mechanism. However, Corriu's data do not support this. Also, Bassindale et al. showed that nucleophilic substitution at silicon involves pentacoordinate intermediates or transition states.[94-96] Bassindale used a model compound, shown in Figure 1.20, that varies between the tetra- and pentacoordinated silicon atom, depending on the nature of the groups X and Y.[94]

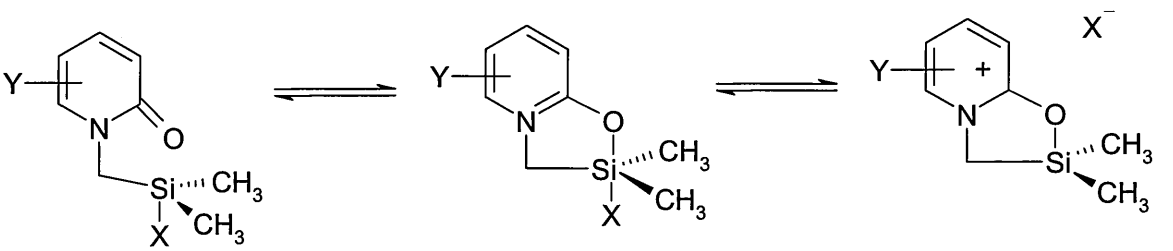


Figure 1.20 A model compound that can be tetracoordinate or pentacoordinate in silicon depending on X and Y

^{29}Si NMR spectroscopy is an important tool for distinguishing between closely related tetracoordinate and pentacoordinate silicon species. Coordination of an additional ligand to tetracoordinate silicon usually results in an upfield shift of between 10 and about 60 ppm. These data along with the ^{13}C NMR spectrum, especially of the six-membered ring in Figure 1.20, which can be used to determine the amount of Si–O bonding, can differentiate between the three proposed structures in Figure 1.20. No Si–O bond was observed when X = OH, but when X = F or Cl, the pentacoordinate species was formed.

The far right structure was formed when X = Br or OSO_2CF_3, where the Si–X bond was broken. The author also noted that as Y is altered to become more electron-donating, then more Si–O bond making is observed for all Xs discussed above. Bassindale et al. further demonstrated the thermodynamic variation between tetracoordinate and pentacoordinate silicon depending upon temperature, using the molecule in Figure 1.21.[97]

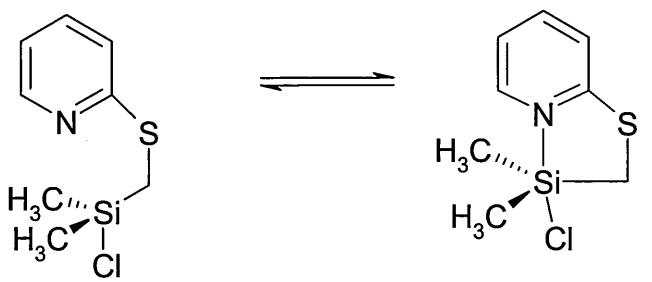


Figure 1.21 A model compound that can be tetracoordinate or pentacoordinate in silicon depending on temperature

At lower temperatures (down to –50°C), the structure shifted toward the pentacoordinated silicon complex. At +50°C, the ^{29}Si shift was –8 ppm compared to TMS, suggesting a tetracoordinate state. When the nucleophile attacked the silicon to form the pentacoordinate state at –50°C the ^{29}Si shift was -31 ppm, as compared to TMS.

The pentacoordinate silicon in trigonal bipyramidal form can internally exchange, or pseudorotate, its ligands. R. Stephen Berry was the first to suggest pseudorotation in the trigonal bipyramid of phosphorous (PCl_5, PF_5).[98] Pseudorotation of the ligands involves rotation of the two axial ligands to the equatorial position, such that two equatorial ligands then take up the axial position, while maintaining the position of the third equatorial ligand, as shown in Figure 1.22.

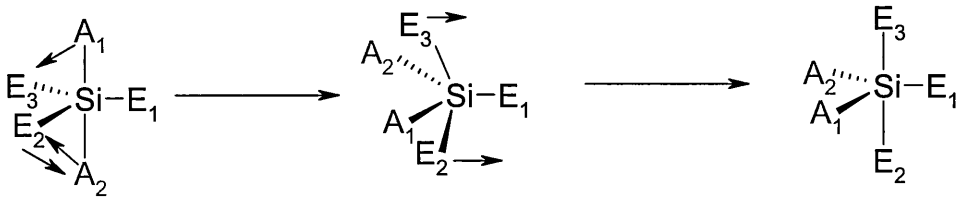
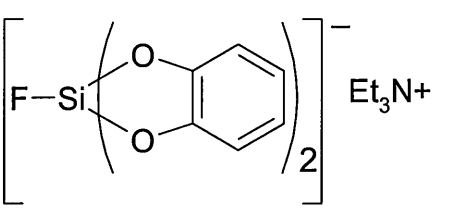


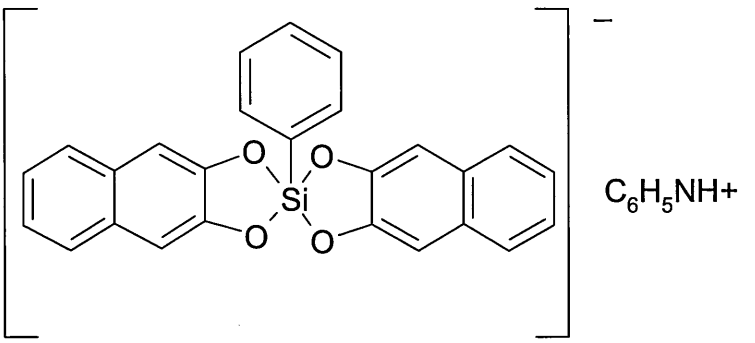
Figure 1.22 Pseudorotation of a silicon pentacoordinate trigonal bipyramid (A=axial, and E = equatorial position of the starting molecule)

Pseudorotation at silicon can thus account for retention of configuration. The nucleophile first enters at the centre of one face to take up the axial position. If the leaving group is not very electronegative, it may assume an equatorial position. Through pseudorotation the leaving group is rotated from the equatorial position to the axial position, and retention of configuration is observed.

While the idealised structure of a pentacoordinated silicon is a trigonal bipyramid, deviations are observed depending on the ligands. When a chiral pentacoordinate silicon is part of a ring structure, a rectangular or square pyramidal configuration is approached.[92] For example, the following compound is displaced by 68.7% from a trigonal bipyramid toward a square pyramidal configuration.[92]



The following compound is even more strained by the phenyl group and is 97.6% displaced from a trigonal bipyramid toward a square pyramidal configuration.



Additionally, retention or inversion can be altered by ring strain where the ring attempts to conform to the 120° or 90° angles in the trigonal bipyramid.

1.6 Summary

Siloxane polymers can be produced by ring-opening polymerisation of cyclosiloxanes (e.g. D_4). Small amounts of acid or base catalyse this reaction. Spielvogel and Frye reported an acid-catalysed transformation of 2,6-diphenylhexamethylcyclotetrasiloxane from one stereoisomer to a 1:1 equilibrium mixture of the *cis* and *trans* stereoisomers. Surprisingly, polymers, oligomers, or other cyclics were not produced, which would have been predicted based on what is known about acid-catalysed ring-opening polymerisation of cyclosiloxanes. The authors suggest two mechanistic pathways to explain this phenomenon. Both of these mechanisms proceed through a ring-opened intermediate. This is interesting because no linear siloxanes or other ring-opened products were observed. Also, if the ring can open at one Si–O bond, it seems possible for this to happen twice, but the 2,6-diphenyl D_4 starting material only produces 2,6-diphenyl D_4 products, and not 2,4-diphenyl D_4 cyclics that one would predict with a ring-opened mechanism. These reactions are carried out in solvent and the starting material contains bulky substituents. Ring-chain equilibria suggest both of these factors lead to a higher concentration of cyclics at equilibrium, thus inhibiting polymer formation.

Frye and Spielvogel's data also suggest that Lewis acids are necessary for this transformation along with a polar aprotic solvent. The role of the proton clearly needs to be explored further.

Finally, more recent research into nucleophilic attack of silicon proceeding through a pentacoordinate intermediate/transition state may have some implications on the mechanism of this interconversion. A pentacoordinate mechanism where the cyclosiloxane ring remains intact would explain why other cyclics, linears, and polymerisation products are not observed. This pentacoordinate intermediate could then pseudorotate to produce the other stereoisomer. This reaction, which takes place at low concentrations of acid, will provide more insight into acid-catalysed ring-opening polymerisation of cyclics. Thus, this rearrangement of cyclic stereoisomers probably occurs first, or more rapidly, than polymerisation, and may explain some of the observations of acid-catalysed ring-opening polymerisation.

The interconversion of 2,6-diphenylhexamethylcyclotetrasiloxane from one stereoisomer to an equimolar mixture of the isomers will be further explored. An understanding of which parameters enhance this interconversion or induce polymerisation will provide mechanistic insights. The kinetic evaluation results of this interconversion catalysed by Brönsted (Chapter 2) and Lewis (Chapter 3) acids will help eliminate possible mechanisms. A pseudorotation mechanism is proposed in Chapter 4 to account for the interconversion without breaking a siloxane bond.

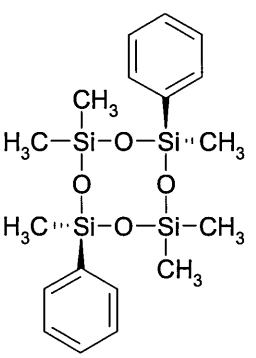
Chapter Two

Interconversion Catalysed by Brönsted Acids

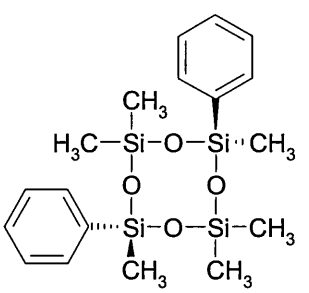
2 Interconversion Catalysed by Brönsted Acids

2.1 Introduction

This chapter will discuss the reactions of a specific D_4 cyclosiloxane, 2,6-diphenylhexamethylcyclotetrasiloxane, catalysed by Brönsted acids. This siloxane molecule has two isomeric forms, shown in Figure 2.1 as *cis* and *trans*. The shorthand of 2,6-*cis* and 2,6-*trans* will be used to refer to the two possible isomers of 2,6-diphenyl-hexamethylcyclotetrasiloxane throughout this document.



2,6-*cis*-diphenylhexamethylcyclotetrasiloxane
2,6-*cis*



2,6-*trans*-diphenylhexamethylcyclotetrasiloxane
2,6-*trans*

Figure 2.1 Isomers of 2,6-diphenylhexamethylcyclotetrasiloxane

The Brönsted-Lowry theory of acids and bases defines an acid as a proton donor and a base as a proton acceptor.[99] Brönsted acids not only supply a proton, but also a potential nucleophile as the conjugate base. The strength of an acid is moderated by this conjugate base, as demonstrated by the difference in acidity of HCl and CH_3COOH. Brönsted acids, such as trifluoromethanesulphonic acid (CF_3SO_3H, commonly referred to as triflic acid), are preferably used today as cyclosiloxane ring-opening polymerisation catalysts because of their stability, solubility, and cost. They are typically more effective than nonprotic Lewis acids, which are defined as any molecule capable of accepting an

electron pair.

Brönsted acids catalyse polymerisation and interconversion of 2,6-diphenylhexamethylcyclotetrasiloxane. Polymerisation occurs through acid catalysed (Figure 2.2) ring-opening, whose detailed mechanism is still not completely understood.[28, 64, 100]

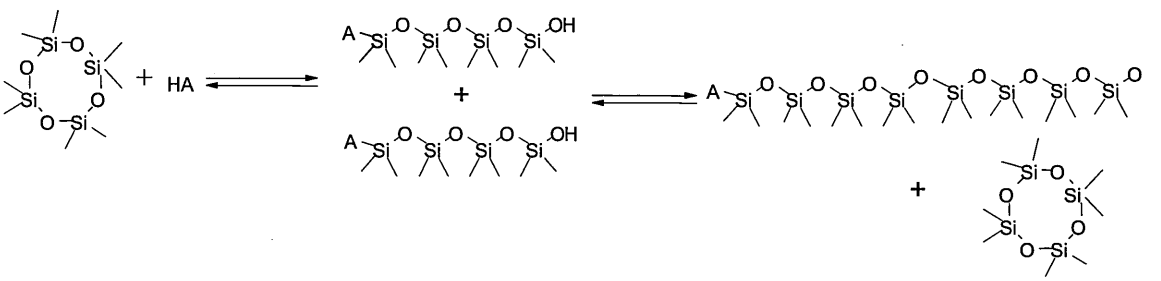
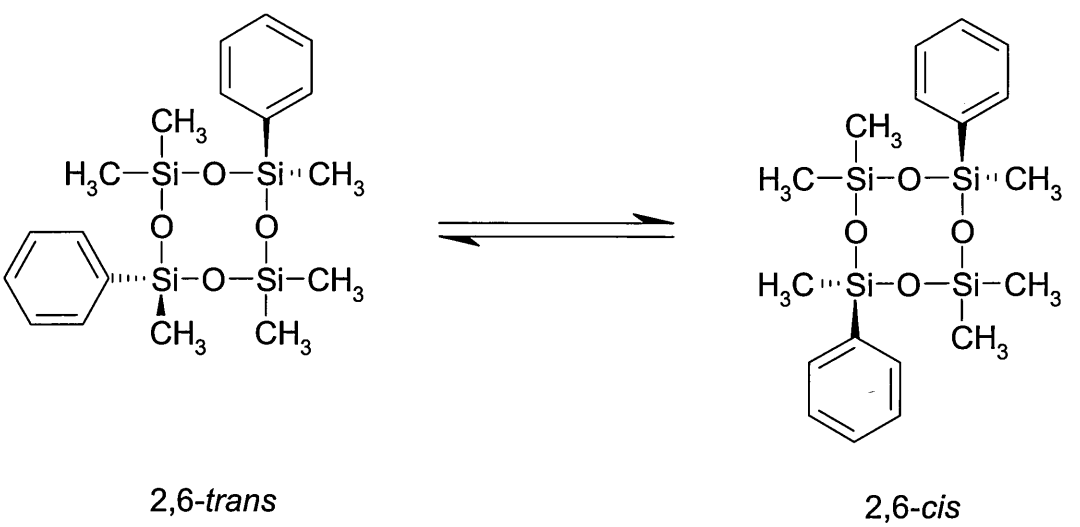


Figure 2.2 Acid catalysed ring-opening polymerisation of cyclosiloxanes

Interconversion describes the transformation from one isomer of 2,6-diphenylhexamethyl-cyclotetrasiloxane to the mixture of two isomers (2,6-*cis* and 2,6-*trans* as shown in Figure 2.3). The research described in this document will focus on the interconversion reaction.



2,6-*trans* 2,6-*cis*

Figure 2.3 Interconversion reaction of 2,6-diphenylhexamethylcyclotetrasiloxane

The degree to which interconversion versus polymerisation occurs varies with temperature, catalyst strength, and catalyst amount, as will be demonstrated. Brönsted

acids of a conjugate base that is strongly nucleophilic toward silicon produced ring-opened polymerisation products, as expected. When the nucleophile was weaker toward silicon, such as trifluoromethanesulphonate anion and methanesulphonate anion, interconversion of the isomers was observed before any appreciable amount of polymerisation, and conditions will be shown where only interconversion was observed. The measurement of both the kinetics of interconversion and that of polymerisation was obtained under conditions where both reactions were operating at a rate that allowed the collection of meaningful data.

2.1.1 Summary of Analytical Method

A gas chromatographic (GC) method was developed to follow the progress of the interconversion reaction from one isomer of 2,6-diphenylhexamethylcyclotetrasiloxane to a mixture of isomers. The GC is a relatively simple and quick (20 minutes or less) method that provides baseline resolution of the 2,6-isomers (*cis* and *trans*) of diphenylhexamethylcyclotetrasiloxane as well as the 2,4-isomers (*cis* and *trans*), if produced. The polar aprotic solvent, nitromethane, was selected based on the successful interconversion results obtained by Frye and Spielvogel (Section 1.4).[80] Naphthalene, which elutes prior to the 2,6-isomers using the GC method, was used as the internal standard and to ensure mass balance. The response factor, R_f, for the 2,6-isomers was determined to be 1.90 + 0.04; details are contained in Section 5.4. The response factor along with the GC area results for naphthalene, 2,6-*cis*, and 2,6-*trans* were used to calculate the concentrations of 2,6-*cis* and 2,6-*trans* according to $C_x=(C_yA_x)/(R_fA_y)$.[101] The equilibrium isomeric product concentrations were used to define the final product mixture and quantify the approach to equilibrium over the entire time length of the reaction. The kinetic data are contained in tables in Appendix A for reactions catalysed by triflic acid

and in Appendix B for reactions catalysed by methanesulphonic acid.

2.1.2 Summary of Kinetic Analysis

The proposed mechanistic pathways and their associated rate equations should be consistent with the observed kinetic order of a reaction, providing insight into the mechanism. For a particular species, the number of concentration factors involved in the rate equation dictates the order of the reaction, where one concentration factor indicates first-order, two indicate second-order, and so forth. The rate of a reaction is often proportional to the concentration of the reactants, and as the reaction proceeds, the rate will decrease, except of course for reactions that are zero-order in a reactant, as this means that the reaction is independent of the concentration of the zero-order reactant. For first-order reactions, this dependence of rate on reactant concentration leads to an exponential decay of reactant concentration with time, assuming the reactant is not present in large excess relative to other reacting species.

The interconversion of either 2,6-isomer led to an equilibrium mixture of approximately 50:50 2,6-*cis*:2,6-*trans*. Since the reaction achieved equilibrium at approximately 50:50 2,6-*cis*:2,6-*trans*, the reaction was followed from 2,6-*cis* reactant to at least 40% 2,6-*trans* (60% 2,6-*cis*) representing 80% reaction. If less than 80% reaction is used to determine the order in the kinetic analysis, there is a risk of falsely assigning the order to what appears to be a linear plot, where any curvature may be missed. A plot of much longer reaction time data than this can lead to further complications, as described below. Interconversion performed under certain conditions produced side reactions or polymerisation, especially after long periods of exposure to elevated temperature or large concentrations of catalyst. The use of these data will interfere with the kinetic analysis of the interconversion, especially if reactant or product concentrations are falsely low due to

consumption by side reactions. The data from the kinetic experiments that used the GC method described above contain a row in the tabulated results which is the sum of the 2,6-stereoisomers and is labelled *cis* + *trans*. The kinetic analysis for interconversion was performed only while this sum was constant, and this mass balance ensured no side reactions had taken place. This was not always possible to obtain due to side reactions, such as polymerisation, etc. that consumed a portion of the reactants and interconversion products. For these reactions, the kinetic analysis was based upon the approach to the experimentally determined equilibrium, 50.2% of the initial starting material concentration for 2,6-*trans* and 49.8% for 2,6-*cis*. This implies 2,6-*trans* is slightly more thermodynamically stable. These percentage values were determined experimentally based on numerous reactions performed under conditions where side reactions did not occur, and the equilibrium amounts were constant after multiple GC analyses (days to months in some instances). These values are the actual equilibrium values determined experimentally, which Frye and Spielvogel reported as approximately 50:50 for the 2,6-isomers.[80] A more detailed discussion on kinetics and reaction order is presented in Section 1.4.1.

2.1.2.1 Method Evaluation for Acid Catalysed Interconversion

Trifluoromethanesulphonic acid induces ring-opening of cyclic siloxanes and is commonly used as a catalyst in cyclosiloxane polymerisation for production of siloxane polymers.[28] The interconversion reaction was attempted with triflic acid over a range of catalyst concentrations in order to refine the analytical method. A solution of 2,6-*cis*, which is a solid under ambient conditions, was dissolved in the polar aprotic solvent nitromethane (CH_3NO_2), then allowed to react in the presence of various concentrations of triflic acid catalyst. Naphthalene was added as an internal standard. The conversion from

2,6-*cis* to an approximately equimolar mixture of the 2,6-*cis* and 2,6-*trans* cyclosiloxanes was followed by the GC method discussed previously. The three GC chromatographs shown (Figure 2.4) follow the progression of the interconversion reaction of 19 mM 2,6-*cis* with time, when catalysed by 1.5 mM triflic acid at 30°C.

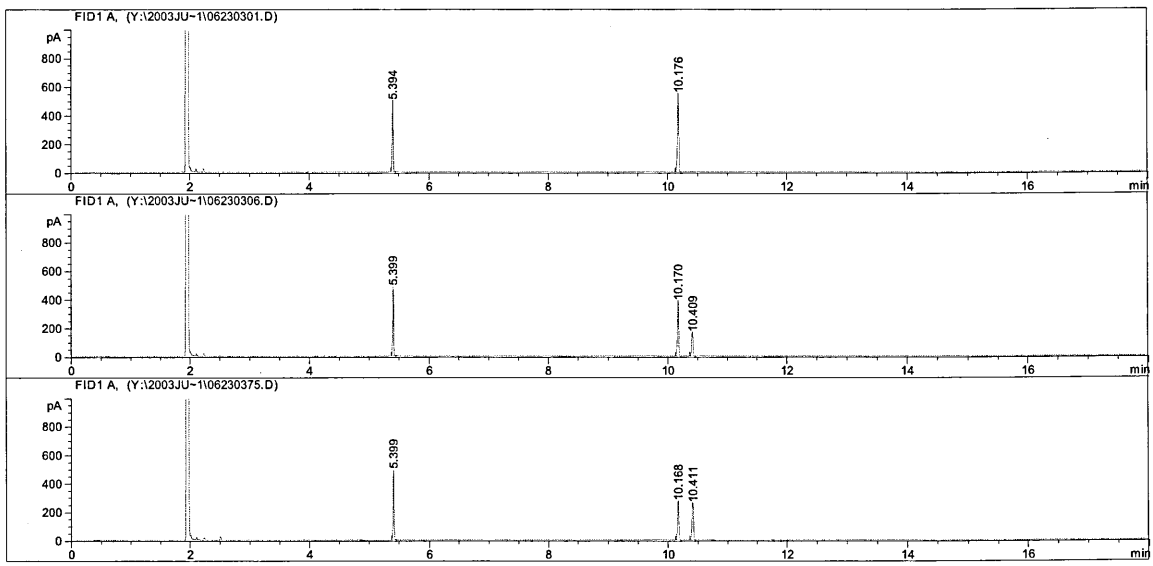


Figure 2.4 Initial, 1.84 hour, and 27 hour elapsed GC traces for the reaction of 19 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.5 mM triflic acid in nitromethane at 30°C (Sample 140-1)

The material eluting at approximately 10.18 minutes represents 2,6-*cis*, the material eluting at 10.41 minutes represents 2,6-*trans*, and that at approximately 5.4 minutes represents the internal standard (naphthalene).

The progression of the interconversion reaction catalysed by several triflic acid catalyst concentrations at 30°C is shown in Figure 2.5, which follows the appearance of the 2,6-*trans* product versus time. The initial concentration of 2,6-*trans* is near zero, and the reaction usually proceeds to an approximate 50:50 mixture of the 2,6-*cis*:2,6-*trans* isomers (49.5 to 49.8% *cis*:50.2 to 50.5% *trans* according to the data in Appendix A).

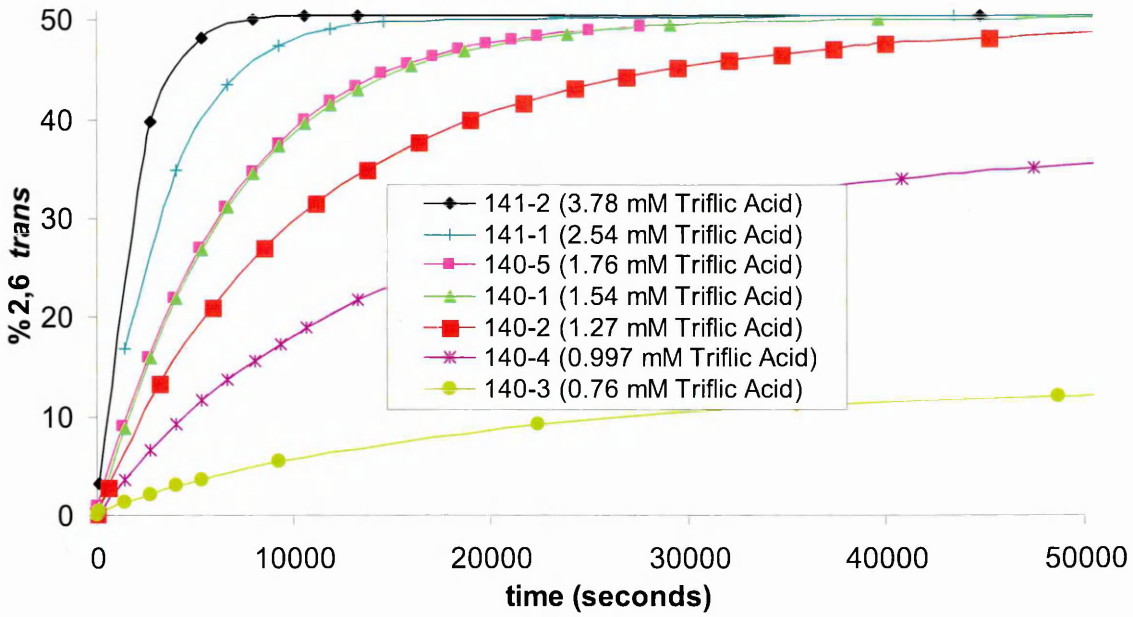


Figure 2.5 Interconversion of 19 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of triflic acid in nitromethane at 30°C

The reaction proceeds to the approximate 50:50 *cis:trans* equilibrium more rapidly with the larger catalyst concentrations 2.5 mM and 3.8 mM triflic acid. The rate of the interconversion reaction is much slower when catalysed by lower catalyst concentrations (less than 1.2 mM triflic acid), and may achieve a different *cis:trans* ratio completion (not the 50.2% 2,6-*trans* observed with the other concentrations). Samples 140-3 and 140-4 do not achieve the 50:50 equilibrium. A side reaction may be consuming the catalyst, which probably occurs in all the reactions, but is more evident in the lower [acid] samples because proportionally a larger percentage of the catalyst is consumed. The amount of acid consumed in the samples that contain a higher [acid] is negligible. The rate of catalyst consumption is faster than the rate of interconversion at low [acid] and slower than interconversion at high [acid].

An examination of the known impurities contained in the solvent did not provide a source of base that could explain the consumption of catalyst, most noticeably observed in

the low [triflic acid] interconversion reactions. Nitromethane (CH_3NO_2) may contain several impurities (water, methanol, ethanol, formaldehyde, nitroalkanes, propionitrile (CH_3CH_2CN), and 1,3,5-trioxane).[102, 103] Water can easily be removed by distillation down to concentrations near 1 x 10^{-3} M due to the formation of a water-nitromethane azeotrope (bp 83°C), where the boiling point of nitromethane is 101.2°C.[104] The azeotrope composition is 76 wt % nitromethane and 24 wt % water.[105] The solvents used in these studies were used as received, and handling precautions as well as physical drying agents (molecular sieves) were used to maintain the dryness of the solvent commercially provided. The concentration of water present in the interconversion system was determined by Karl Fischer titration (see Section 5.3 for method details). The nitromethane solvent contained approximately 50 ± 5 ppm of water. The dissolution of small amounts of siloxane in nitromethane did not alter this 50 ppm value, which indicates that the siloxane did not bring significant amounts of water with it.

The other nitroalkane impurities (namely nitroethane and nitropropane) do not significantly impact the properties of the solvent (only the viscosity and density) and in the concentrations observed have no meaningful impact on the reactivity of the solvent. Bardin identified nearly 10^{-1} M propionitrile (CH_3CH_2CN) in nitromethane.[103] The interconversion reaction has been successfully performed in acetonitrile solvent, so small amounts of propionitrile impurity is not likely to be basic enough to consume the acid. In 2005, Huang and Bien reported the contaminant 1,3,5-trioxane in nitromethane as the cause for the formation of a new dimer in their acidic ($AlCl_3$) conditions.[106] Pearson and Dillon reported a rate constant of 3.7 x 10^{-8} s^{-1} for the reaction of nitroethane with water and an acid strength of K_a = 2.5 x 10^{-9}.[107] Parrett and Sun provide a method for removal of other nitroalkanes (nitroethane, nitropropane) as well as propionitrile from nitromethane by crystallisation from cold (–60°C to –78°C) diethyl ether to produce 99.9% pure

nitromethane according to ^{13}C NMR.[108] The presence of water and a base in the nitromethane solvent are a concern with the acid catalysed interconversion reactions studied. A minor basic impurity in the solvent would easily consume the acid catalyst, as the catalyst concentrations studied are small (1 mM). We postulate the nitromethane solvent contains a small amount of a basic impurity, possibly an amine (RNH_2).

The GC data from the triflic acid catalysed interconversion reaction (GC results shown in Figure 2.5) are shown in Table 2.1 for reactions of 2,6-*cis* with 1.5 mM triflic acid. Data for the remainder of the reactions with triflic acid are contained in tables in Appendix A.

140-1 (1.54 mM Triflic Acid)	time (sec)	0	64	1375	2688	4001	5315	6629	7943	9257
	% 2,6-*trans*	0	0.8	8.7	15.9	21.9	26.9	31.0	34.5	37.3
GC area Naphthalene			578.6	579.5	577.8	576.7	575.4	576.0	572.9	570.8
GC area 2,6-*cis*			893.7	812.1	746.3	690.5	644.6	607.7	576.1	549.5
GC area 2,6-*trans*			7.0	77.8	141.3	193.5	237.1	273.6	303.3	327.0
Conc. 2,6-*cis*	(mol/L)		0.0210	0.0190	0.0175	0.0163	0.0152	0.0143	0.0137	0.0131
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0018	0.0033	0.0046	0.0056	0.0065	0.0072	0.0078
ln [*trans* eq/*trans* eq-*trans* t]			0.0158	0.1907	0.3802	0.5690	0.7612	0.9527	1.1541	1.3504
ln [*cis* t-*cis* eq]			-4.54	-4.74	-4.93	-5.12	-5.32	-5.51	-5.70	-5.89
cis + *trans*	(mol/L)		0.0211	0.0209	0.0209	0.0208	0.0208	0.0208	0.0208	0.0209
1/(*cis* t-*cis* eq)			93.69	114.56	138.14	167.83	203.58	248.37	298.08	360.72
1/(*trans* eq-*trans* t)			96.75	115.25	139.29	168.24	203.89	246.91	302.01	367.53

140-1 (1.54 mM Triflic Acid)	time (sec)	10573	11888	13204	15992	18622	23881	29138	39652
	% 2,6-*trans*	39.6	41.5	43.0	45.4	46.9	48.6	49.5	50.1
GC area Naphthalene		571.9	573.5	570.1	571.7	571.3	574.3	569.1	568.0
GC area 2,6-*cis*		530.1	515.0	498.4	477.4	463.2	449.8	441.5	433.6
GC area 2,6-*trans*		347.8	365.3	376.3	396.4	408.7	425.5	431.9	435.6
Conc. 2,6-*cis*	(mol/L)	0.0126	0.0122	0.0119	0.0113	0.0110	0.0106	0.0105	0.0104
Conc. 2,6-*trans*	(mol/L)	0.0083	0.0086	0.0090	0.0094	0.0097	0.0101	0.0103	0.0104
ln [*trans* eq/*trans* eq-*trans* t]		1.5440	1.7358	1.9215	2.2700	2.5924	3.1739	3.9877	4.8015
ln [*cis* t-*cis* eq]		-6.08	-6.27	-6.46	-6.87	-7.25	-8.00	-8.36	-9.63
cis + *trans*	(mol/L)	0.0208	0.0208	0.0208	0.0208	0.0207	0.0207	0.0208	0.0208
1/(*cis* t-*cis* eq)		437.36	528.03	636.47	962.33	1409.30	2983.06	4266.91	15174.35
1/(*trans* eq-*trans* t)		446.03	540.34	650.58	921.87	1272.57	2276.19	5136.16	11589.35

Table 2.1 GC data for the interconversion reaction of 19 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.54 mM triflic acid in nitromethane at 30°C.

2.1.2.2 Reaction Order

The initial concentration of the reactant is known, and a plot based on the integrated rate equation according to first-order kinetics is possible. According to Section 1.4.1 the plot of logarithm of concentration of the reactant versus time will produce a straight line if first-order kinetics is operating. A first-order rate constant implies that only one molecule of the starting material is participating in the mechanism in or before the rate-determining step of this reaction. First-order with respect to either D_3 or D_4 cyclosiloxane starting material has been observed by other researchers with triflic acid catalysed polymerisation.[64,66] The determination of the reaction order ($J = k$ [2,6-*cis*]^x [catalyst]^y) will define how many molecules are involved in the rate determining step of the reaction mechanism.

For the interconversion reaction, the loss of the starting material, 2,6-*cis* isomer, was plotted versus time (Figure 2.6). According to first-order kinetics, if ln [reactant] is plotted against time the slope of the resulting line represents the negative rate constant ($-k$). This is shown in Figure 2.6 for the interconversion (Sample 140-1) of 19 mM 2,6-*cis* catalysed by 1.5 mM triflic acid in nitromethane solvent at 30°C (Table 2.1). Good linearity is shown by a best-fit correlation in Figure 2.6 ($R^2 = 0.999$).

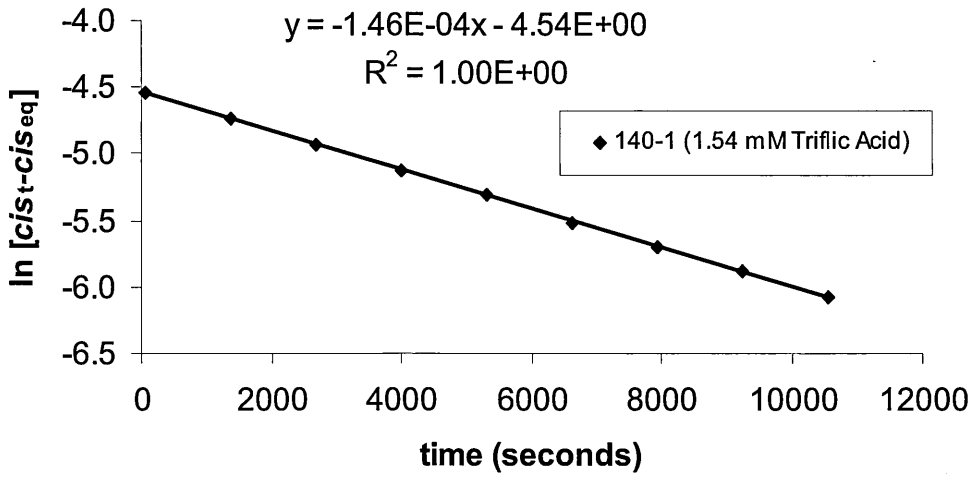


Figure 2.6 Interconversion of 19 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.54 mM triflic acid in nitromethane at 30°C according to first-order kinetic law, where GC data show the loss of the [2,6-*cis*] isomer

This reaction begins with 99% pure 2,6-*cis* and was followed to equilibrium; an approximate 50:50 mixture of isomers. The loss of the starting material (2,6-*cis*) would commonly be analysed in the kinetic evaluation of a reaction where A (reactant) goes to B (product). In these interconversion reactions, the concentration at time *t* of the starting material minus the equilibrium concentration (2,6-cis_t–2,6-cis_{eq}) must be analysed, since the reaction achieves equilibrium with approximately 50% of the starting material remaining. The reaction can be monitored by tracking either the loss of the 2,6-*cis* isomer reactant or the production of 2,6-*trans*. If no other products are formed, the rate of 2,6-*cis* loss and 2,6-*trans* production should be equivalent. This can be validated with an internal standard method that accounts for mass balance, where the production of the 2,6-*trans* isomer is monitored by ($trans_{eq}/trans_{eq}$–$trans_t$). The rate constant at which 2,6-*cis* is lost (1.46×10^{-4} s^{-1}, from the slope in Figure 2.6) was found to equate to that obtained from the production of the 2,6-*trans* isomer (1.46×10^{-4} s^{-1}, in Figure 2.7), as expected. This is consistent with no loss of material to non-volatile products.

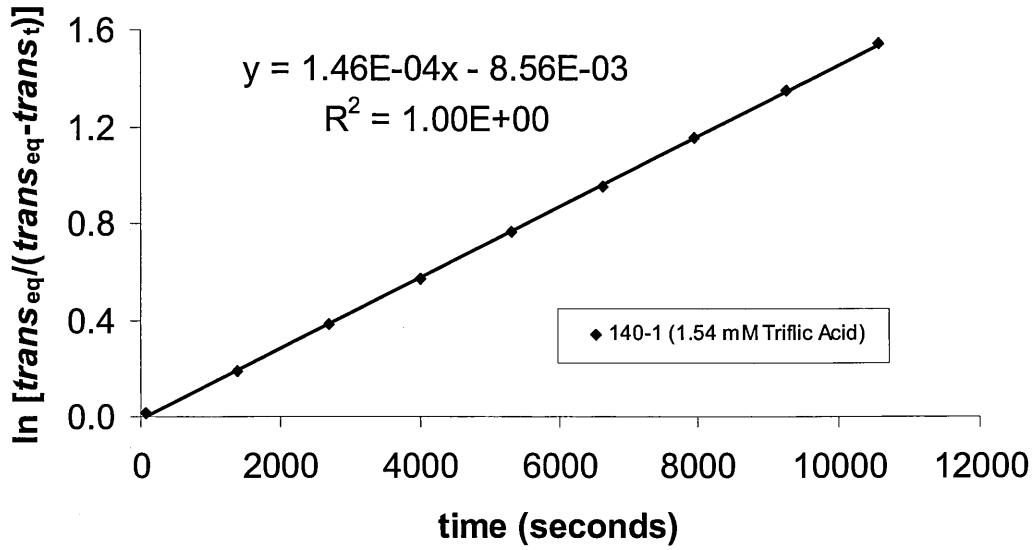


Figure 2.7 Interconversion of 19 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.54 mM triflic acid in nitromethane at 30°C, where GC data show the production of the [2,6-*trans*] isomer

The excellent linearity of the loss of 2,6-*cis*, as shown in the plot of $\ln[cis_t\text{-}cis_{eq}]$ versus time, suggests that this interconversion is first-order in 2,6-*cis* starting material. The similar rate constant for the production of 2,6-*trans* indicates mass balance is maintained and only interconversion products are formed. For the rate equation, $x = 1$ for the order in 2,6-*cis* starting material according to $J = k\,[2,6\text{-}cis]^x\,[\text{catalyst}]^y$. An analysis of the same data using a second-order rate law was completed for comparison. If second-order kinetics is obeyed for a single reactant the plot of the inverse of the concentration of the reactant versus time will produce a straight line (see *Second-order Kinetics* in Section 1.4.1.1 for more detail). Figure 2.8 shows the loss of the 2,6-*cis* isomer plotted as $1/[2,6\text{-}cis_t\text{–}cis_{eq}]$ versus time, along with a best-fit line.

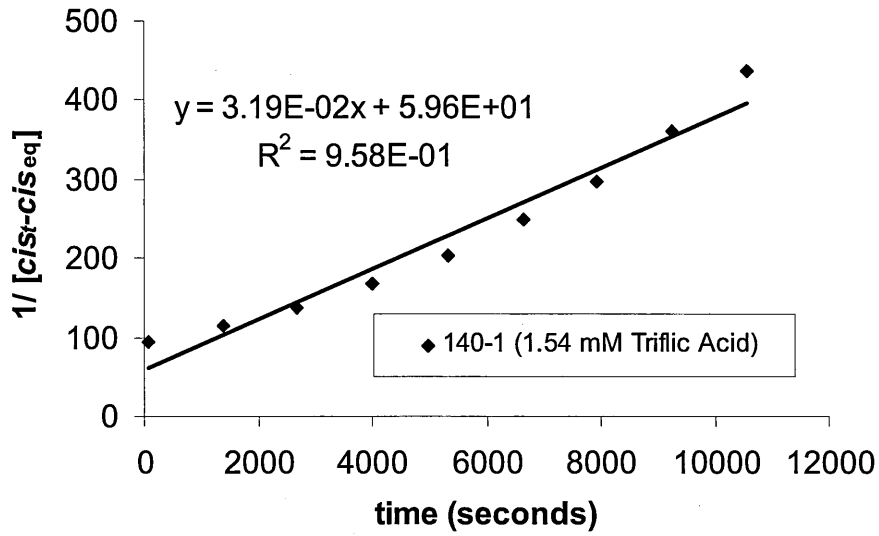


Figure 2.8 Interconversion of 19 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.54 mM triflic acid in nitromethane at 30°C according to second-order kinetic law, where GC data show the loss of the [2,6-*cis*] isomer

The poor linear fit (Figure 2.8) suggests second-order kinetics is not likely to be operating, and first-order in reactant (2,6-*cis*) is appropriate.

The interconversion of 19 mM 2,6-*cis* catalysed by the other triflic acid concentrations (Figure 2.5) was evaluated based on first-order kinetics. These results are shown in Table 2.2. (Note: The results from 0.76, 2.54, and 3.78 mM triflic acid catalysed interconversion were not used in the following kinetic calculations. The 0.76 mM triflic acid data were not used because the reaction was very slow and did not go to completion over the studied reaction time. Reactions catalysed by 2.54 and 3.78 mM triflic acid proceeded too quickly to allow enough data points to be collected, before 80% conversion, to allow meaningful kinetic analysis.)

Sample #	[triflic acid] (mM)	*k* (1/sec) (-loss of 2,6-*cis*)	*k* (1/sec) (production of 2,6-*trans*)	R^2 (production of 2.6-*trans*)
140-5	1.76	1.51E-04	1.50E-04	0.9995
140-1	1.54	1.46E-04	1.46E-04	0.9998
140-2	1.27	8.24E-05	8.27E-05	0.9987
140-4	1.00	3.97E-05	3.99E-05	0.9926

Table 2.2 Rate constants for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of triflic acid in nitromethane at 30°C.

This method was used throughout this chapter to calculate the rate constant of the interconversion reactions based on first-order kinetics. The rate constants based on the loss of 2,6-*cis* are plotted as a function of acid concentration to show the impact catalyst concentration has on the rate constant at 30°C (Figure 2.9).

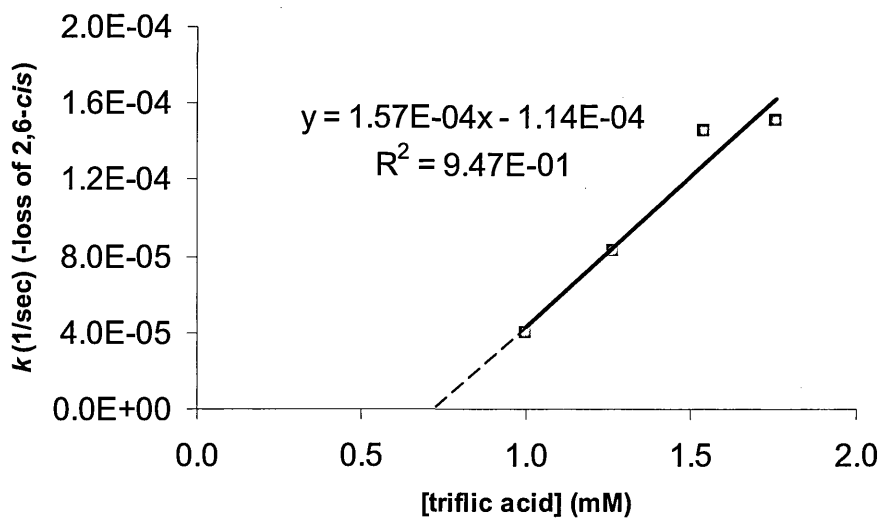


Figure 2.9 Rate constant versus concentration of triflic acid for 19 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of triflic acid in nitromethane at 30°C.

The x-intercept based on the best-fit line is 0.73 mM triflic acid, which implies that a threshold concentration of catalyst is required to initiate the reaction. A similar level of catalyst, 0.72 mM, was required based on the *x*-intercept of the best-fit line of the data

based on the production of 2,6-*trans* isomer (Figure 2.10).

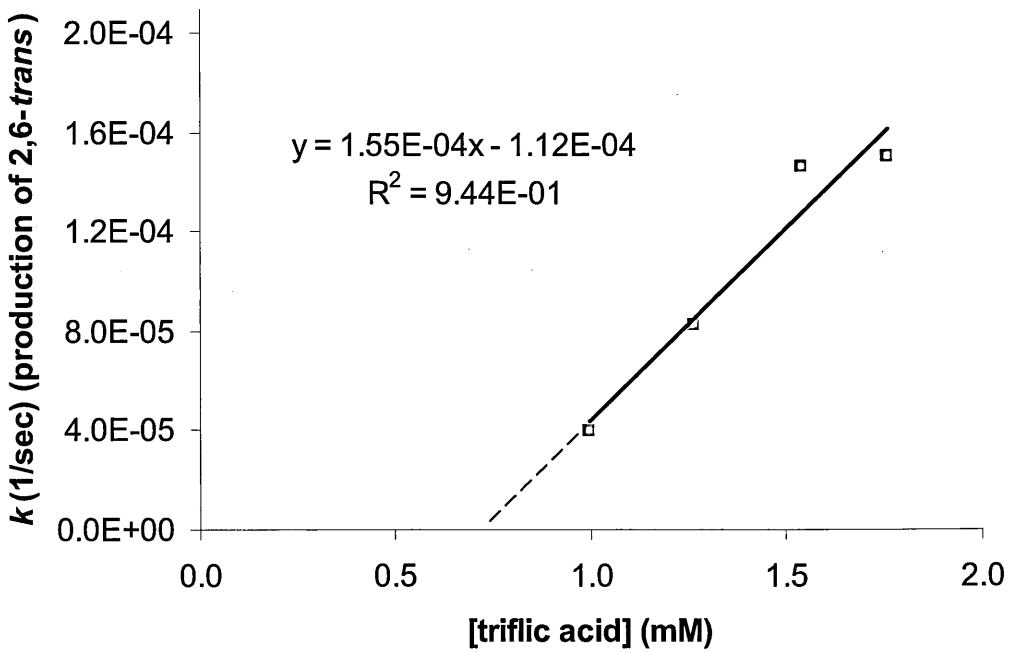


Figure 2.10 Rate constant versus concentration of triflic acid catalyst used for the interconversion reaction of 19 mM 2,6-*cis*-diphenylhexamethyl-cyclotetrasiloxane catalysed by various concentrations of triflic acid in nitromethane at 30°C.

A "corrected" acid concentration can be calculated by subtracting the extrapolated inactive catalyst concentration (Figure 2.9, Figure 2.10) from the initially added amount of catalyst. This value should better reflect the concentration of active catalyst in reaction solutions that is available for catalysing the interconversion reaction (Table 2.3).

Sample #	[triflic acid] (mM)	[2,6-*cis*] (mM)	corrected [acid] (mM)	ln (corrected [acid])
140-5	1.76	19	1.03	-6.88
140-1	1.54	19	0.81	-7.11
140-2	1.26	19	0.53	-7.53
140-4	1.00	19	0.27	-8.23

Sample #	*k* (1/sec) (-loss of 2,6-*cis*)	*k* (1/sec) (production of 2,6-*trans*)	ln *k* (-loss of 2,6-*cis*)	ln *k* (production of 2,6-*trans*)
140-5	1.51E-04	1.41E-04	-8.80	-8.87
140-1	1.46E-04	1.43E-04	-8.83	-8.85
140-2	8.24E-05	8.05E-05	-9.40	-9.43
140-4	3.97E-05	3.59E-05	-10.1	-10.2

Table 2.3 Rate constants for the interconversion reaction of 19 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of triflic acid in nitromethane at 30°C, including corrected [acid].

There are many possible explanations for the limiting concentration of catalyst required before interconversion is observed. An impurity in the solvent or reactant (possibly a base) could be reactive towards the catalyst and consume a portion of it. Sigwalt et al. showed an inhibition in the initial rate of D_4 polymerisation (R_{po}) catalysed by triflic acid and the apparent rate constants ($k_{app} = k_p[P^*]$), based on the first-order plot of monomer consumption, with the addition of water (Table 2.4).[109]

	$[D_4]_0$ mol/l	$[TfOH]_0 \times 10^{-3}$ mol/l	$[H_2O]_0$ / $[TfOH]_0$	$R_{po} \times 10^{-3}$ mol/l sec	$k_{app} \times 10^{-3}$ 1/sec
no water added	0.97	5.8	N/A	0.64	0.33
water mixed *in situ*	0.96	5.8	1	0.37	0.23
water mixed *in situ*	0.97	5.8	10	0	0 (-->4h)
no water added	0.91	1.6	N/A	0.16	0.1
water premixed with TfOH	0.91	1.56	1	0.013	0.02

Table 2.4 Effect of water mixed into the reaction solution or premixed with the catalyst on initial rate R_{po} in the polymerisation of D_4 by triflic acid in CH_2Cl_2 at 20°C, reproduced from Table III in Reference 109

The order in triflic acid was determined to be third order. The reaction rate slowed when a 1:1 water to catalyst ratio was used. When a 10x excess of water to acid was used, no appreciable polymerisation was observed over 4 hours. Water has a large impact on the rate of polymerisation, and depending on the amount of water, the rate can be increased or

decreased. The role of water is discussed in more detail in Chapter 3.

The order of a reaction with respect to a reactant or catalyst can be determined by plotting the log of the concentration of that reactant versus the log of the rate constant. The slope of the best-fit line should equate to the order with respect to the catalyst. The corrected catalyst concentration was used for these calculations (Figure 2.11).

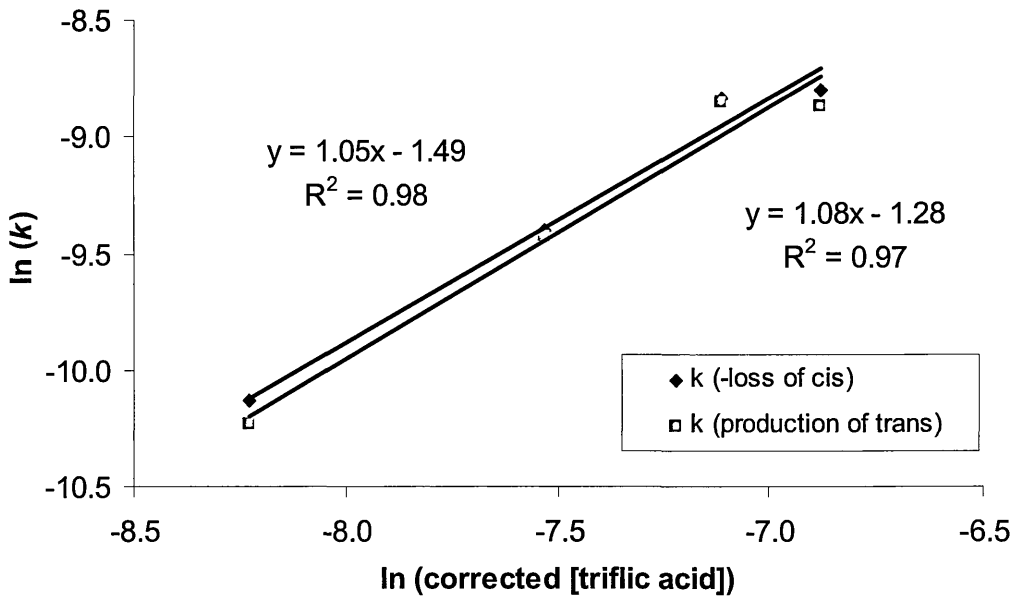


Figure 2.11 Rate constant data for the interconversion reaction of 19 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by triflic acid in nitromethane at 30°C.

The slope of the linear fit (Figure 2.11) is 1.05 and 1.08 for the rate constant of interconversion based on the loss of 2,6-*cis* and the production of 2,6-*trans*, respectively, at 30°C, confirming that the kinetics of interconversion under these conditions is best described as first-order in catalyst.

2.1.2.3 Formation of Other Materials/Polymerisation

Although the *cis-trans* isomerisation reactions with higher concentrations of catalyst achieve equilibrium more rapidly, as expected, side reactions, such as

polymerisation, also occur more rapidly. High concentrations (e.g. greater than 1 mM at 30°C) of triflic acid catalyse the interconversion, but other materials can form after the approximate 1:1 ratio of 2,6-*cis*:2,6-*trans* has been achieved. If only interconversion between 2,6-*cis* and 2,6-*trans* has occurred, then the sum of the concentration of the two isomers should be constant, and thus a horizontal line would be produced (Figure 2.12) when plotted against time.

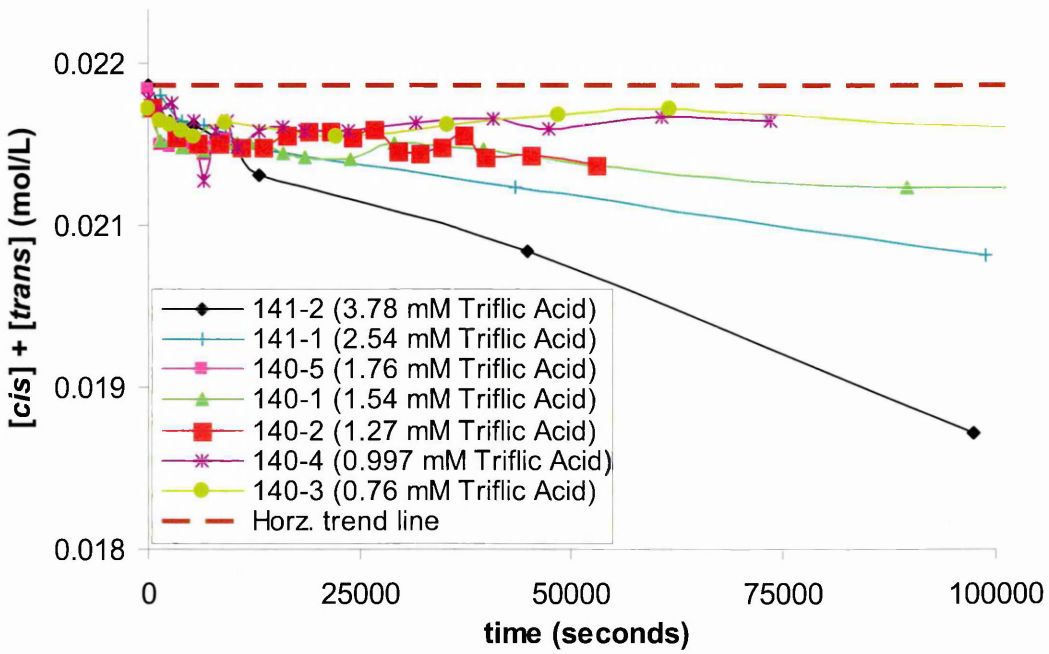


Figure 2.12 Total concentration of the two isomers (*cis* and *trans*) according to GC data from the interconversion reaction of 19 mM 2,6-*cis*-diphenylhexamethyl-cyclotetrasiloxane catalysed by 0.76 to 3.78 mM triflic acid in nitromethane at 30°C.

The amount of [2,6-*cis*] + [2,6-*trans*] is relatively constant when catalysed by lower concentrations of triflic acid (< 1 mM), while the higher acid concentrations (> 1.5 mM) show a decrease in the sum of the isomers over a period of time. This suggests other materials are being formed, while the equilibrium (approximately 1:1) ratio of 2,6-*cis* and 2,6-*trans* appears to remain constant (Figure 2.5, and GC data in Appendix A).

Interconversion appears to be relatively fast with these higher acid concentrations. The study of interconversion was performed using lower triflic acid concentrations to slow the rate of polymerisation so useful interconversion data could be gathered before the products were masked by polymerisation. During polymerisation, cyclosiloxanes may be formed from interconversion or from redistribution reactions.

2.1.2.4 Source of Catalyst Consumption: Reaction Vessel

A study specifically designed to determine the cause of the consumed or "inactive" catalyst was not undertaken, but several steps to increase accuracy and especially to eliminate moisture were implemented. A reaction vessel study showed that the moisture/silanol content on certain untreated glass GC vials reduced the concentration of active catalyst toward interconversion. The type of GC vial surface was examined in an attempt to determine possible causes of the premature consumption of the catalyst. It was postulated that untreated glass vials may provide a source of moisture or silanol, which could consume the catalyst, especially with Lewis acids. In order to test this hypothesis, three types of vials were evaluated. The treatment procedure is described in Section 5.4.2, and the findings are summarised in Table 2.5.

Sample	[triflic acid] (mM)	[2,6-*cis*] (mM)	*k* (mol/l s)	*k*/ [triflic acid] (mol/l s)
144-1 GC vial	1.00	19.0	1.90E-05	1.00E-03
144-2 HMDZ silylated vial	1.01	19.2	2.70E-05	1.41E-03
144-3 Agilent pre-treated silanised vial	1.02	19.2	3.00E-05	1.56E-03

Table 2.5 Comparison of reaction rate constants calculated from GC data for the interconversion reaction of 19 mM 2,6-*cis*-diphenylhexamethyl-cyclotetrasiloxane catalysed by triflic acid in nitromethane at 30°C using treated and untreated GC vials

The results of this study showed a significant difference in the rate constant of comparative interconversion reactions when carried out in the different vials. The untreated vials showed a 30 to 37% decrease in the rate constant of 2,6-*cis* interconversion

catalysed by triflic acid when compared to hexamethyldisilazane-treated GC vials. This is presumably because some triflic acid (tfOH) is consumed or deactivated with the untreated vials (e.g. $H_3O^+ + {}^-Otf$), based on first-order in catalyst for each reaction. Only a small difference was observed between the hexamethyldisilazane-treated vials purchased from Agilent pre-treated, and those treated in our laboratory. The previous studies were performed in untreated vials, and Agilent pre-treated "silanised" vials as received from the manufacturer were used for the rest of the experiments in this chapter. Next, various protic acids were evaluated as catalysts for the interconversion reaction, now that the method had been established.

2.2 Nucleophiles for Cyclosiloxane Ring-Opening

Strong protic mineral acids (e.g. H_2SO_4, HCl) are often used in the polymerisation and redistribution of cyclosiloxanes.[4] These Brönsted acids protonate the siloxane oxygen of a cyclosiloxane, followed by nucleophilic attack on an adjacent silicon atom, thus opening the siloxane ring to form a reactive linear siloxane. The formed linear siloxanes act as polymerisation centres for chain propagation and scission, as discussed in Section 1.3.3, to form polysiloxanes.

A concentration of protic acid catalyst greater than 1 mM is typically used for polymerisation of cyclosiloxanes. Similar catalyst concentrations ($\leq$1 mM) and concentrations lower than those typically used for polymerisation of cyclosiloxanes were used in our study in order to slow the reaction rate sufficiently to obtain useful results for kinetic analysis, especially that of the interconversion reaction. High catalyst concentrations are known to cause rapid polymerisation of cyclosiloxanes, even under interconversion conditions (e.g. polar aprotic solvent). Frye and Spielvogel's attempts with low concentrations of sulphuric acid (H_2SO_4) resulted in the partial conversion from

the 2,6-*trans* isomer to the 2,6-*cis* isomer, but rearranged 2,4-isomers were also observed.[80] As previously discussed, Frye and Spielvogel showed interconversion of 2,6-*trans* to an approximate 50:50 mixture of 2,6-*cis* and 2,6-*trans* isomers only using *Lewis acids* in nitroalkane (polar aprotic) solvents without the production of any other siloxanes. Their attempts at interconversion catalysed by protic acids, without the complication of other reactions, were not successful.

Our attempts at interconversion with protic acids that have conjugate bases that are strongly nucleophilic to silicon centres resulted in polymerisation similar to that reported by Frye and Spielvogel with H_2SO_4. In our work the strongly nucleophilic catalysts H_2SO_4, HCl, and HNO_3 were evaluated over a temperature range of 40 to 70°C. Ring-opening polymerisation of the 2,6-*cis* starting material was observed under all conditions attempted with these catalysts. For example, a sample of 12.8 mM 2,6-*cis* in nitromethane was heated in the presence of 1.21 mM sulphuric acid at 60°C. The GC method detailed in Section 5.4 was used to follow the progress of the reaction. The initial GC chromatogram is shown in Figure 2.13, where the material eluting at 10.18 minutes represents 2,6-*cis* and that at 5.39 minutes represents the internal standard (naphthalene).

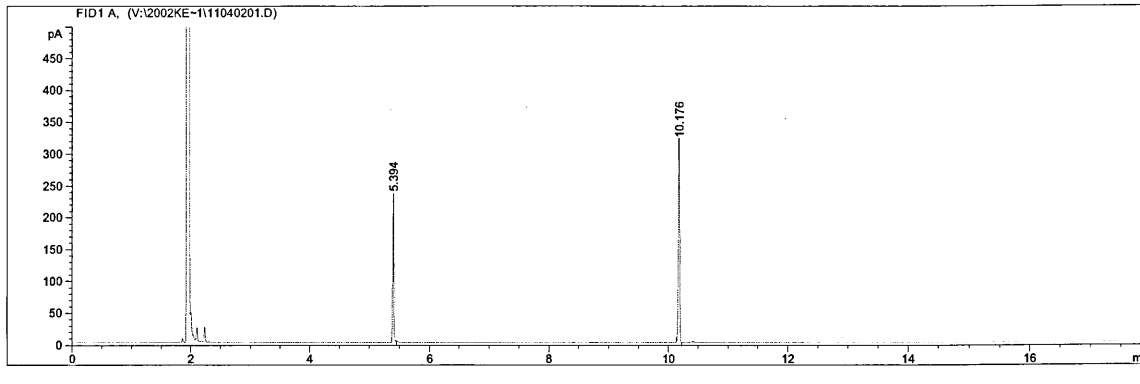


Figure 2.13 Initial GC trace for the reaction of 12.8 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.21 mM sulphuric acid in nitromethane at 60°C.

The 2,6-*trans* isomer product is monitored (Figure 2.14) at 10.41 minutes, but other

unidentified materials are formed concurrently.

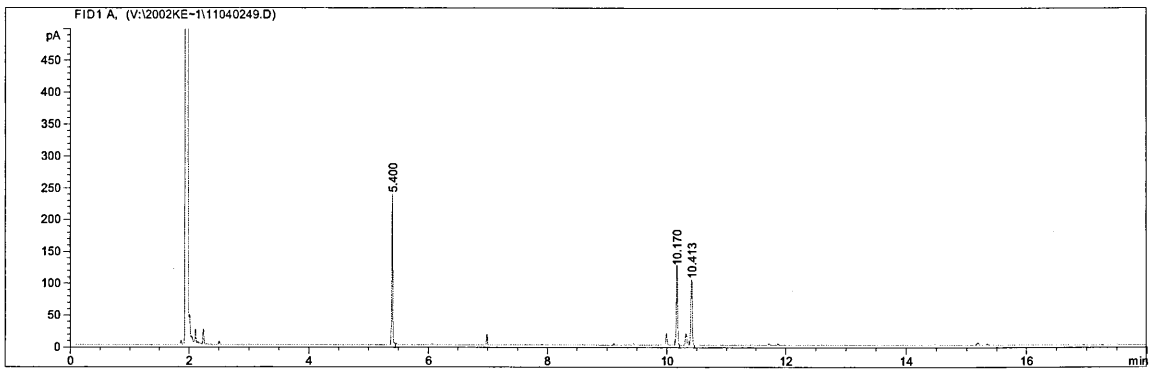


Figure 2.14 GC trace for the reaction of 12.8 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.21 mM sulphuric acid in nitromethane at 60°C after 63272 seconds (~18 hours).

The peaks of other species observed in the chromatograph (Figure 2.14) at slightly shorter and longer retention times than the 2,6-*cis* starting material appear larger in the approximate 86 hour GC trace (Figure 2.15). Also, the 2,6-*cis* and 2,6-*trans* peaks have been significantly reduced when compared to the internal standard eluting at 5.4 minutes (Figure 2.15). The small peak at just less than 10.17 minutes and the peak between the peaks at 10.17 and 10.42 minutes are consistent with the 2,4-isomers of diphenylhexamethylcyclotetrasiloxane (order of elution is 2,4-*cis*, 2,6-*cis*, 2,4-*trans* , 2,6-*trans*).[110]

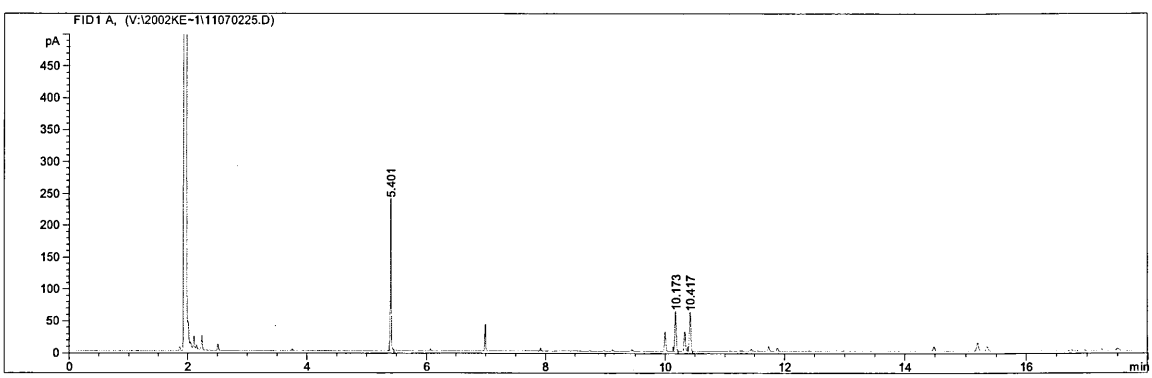


Figure 2.15 GC trace for the reaction of 12.8 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.21 mM sulphuric acid in nitromethane at 60°C after 308457 seconds (~86 hours).

The data for this reaction are contained in Table 2.6, where the last column depicts the amount of 2,6-isomers. This is an indication of how much 2,6-isomers remain, where a value of 100% indicates no ring-opened products or any materials other than the 2,6-isomers have been produced. The last entry in the last column shows that greater than 60% of the 2,6-isomers have disappeared—only 39% remain after approximately 86 hours (5141 minutes) of reaction. The amount of 2,6-isomers would remain constant at 100% if only the interconversion reaction were operating.

Time (minutes)	Time (seconds)	[2,6-*cis*] (M)	[2,6-*trans*] (M)	*2,6-cyclics Sum* [*2,6-cis*] + [*2,6-trans*] (M)	*Approach to Equilibrium* % 2,6-*trans* of total 2,6-cyclics (%)	*Mass Balance* % 2,6-cyclics of initial 2,6-cyclics sum (%)
2.5	150	0.0152	0.0000	0.0152	0	100
1054.5	63272	0.0058	0.0050	0.0108	46	71
5141	308457	0.0030	0.0029	0.0059	50	39

Table 2.6 GC data for the reaction of 12.8 mM 2,6-*cis*-diphenylhexamethyl-cyclotetrasiloxane catalysed by 1.21 mM sulphuric acid in nitromethane at 60°C.

In a second reaction, 12.8 mM 2,6-*cis* in nitromethane was catalysed by a larger concentration of sulphuric acid (6.06 mM) at 60°C. The first GC chromatograph collected after the catalyst is added is labelled initial (Figure 2.16).

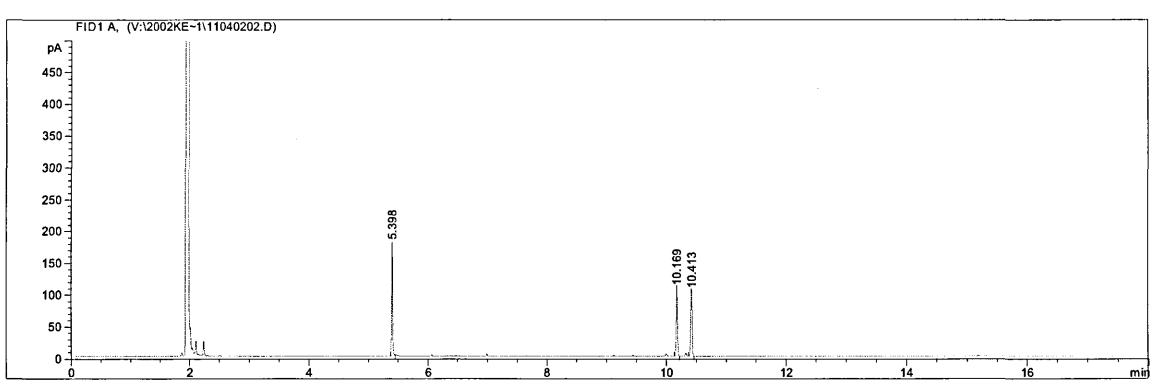


Figure 2.16 Initial GC trace for the reaction of 12.8 mM 2,6-*cis*-diphenylhexamethyl-cyclotetrasiloxane catalysed by 6.06 mM sulphuric acid in nitromethane at 60°C.

Some interconversion has taken place rapidly (Figure 2.16) with this larger concentration

of catalyst. After approximately 86 hours, the GC chromatograph (Figure 2.17) shows the disappearance of most of the 2,6-cyclics and the appearance of many other peaks.

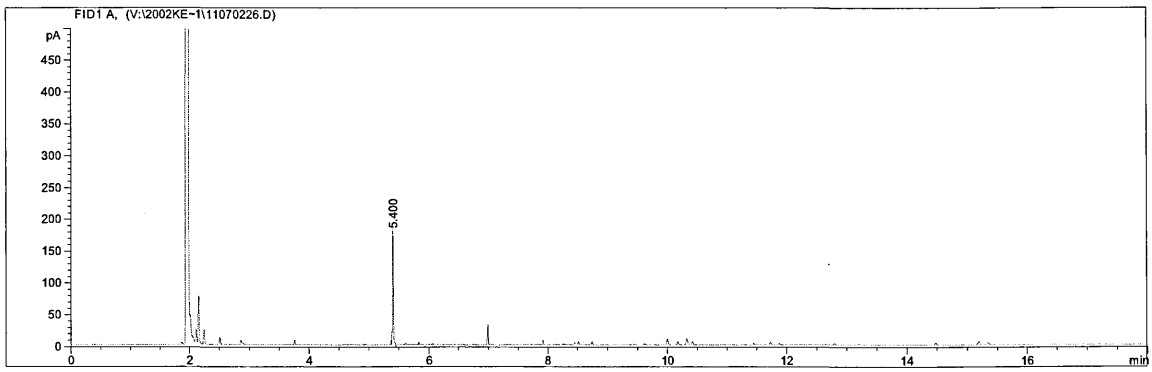


Figure 2.17 GC trace for the reaction of 12.8 mM 2,6-*cis*-diphenylhexamethyl-cyclotetrasiloxane catalysed by 6.06 mM sulphuric acid in nitromethane at 60°C after 309774 seconds (~86 hours).

Table 2.7 shows the GC data from the above reaction, where a loss of approximately 96% of the total 2,6-cyclics (4% 2,6-cyclics remaining after 5162.9 minutes) has occurred.

Time (minutes)	Time (seconds)	[2,6-*cis*] (M)	[2,6-*trans*] (M)	*2,6-cyclics Sum* [2,6-*cis*] + [2,6-*trans*] (M)	*Approach to Equilibrium* % 2,6-*trans* of total 2,6-cyclics (%)	*Mass Balance* % 2,6-cyclics of initial 2,6-cyclics sum (%)
24.3	1459	0.0064	0.0065	0.0129	50	100
5162.9	309774	0.0003	0.0003	0.0006	50	4

Table 2.7 GC data for the reaction of 12.8 mM 2,6-*cis*-diphenylhexamethyl-cyclotetrasiloxane catalysed by 6.06 mM sulphuric acid in nitromethane at 60°C.

The 2,6-*cis* reactant when catalysed by sulphuric acid did not proceed only to interconversion products (i.e. a mixture of only 2,6-*trans* and 2,6-*cis* was not observed). As the reaction proceeded, the GC peaks assigned to the lower molecular weight siloxanes progressively disappeared relative to the internal standard, suggesting non-volatile polymeric products were formed. This is consistent with the previous reports of ring-opening cyclosiloxane polymerisation. Similar results were observed when 2,6-*cis* was

catalysed by aqueous HCl or HNO_3 in nitromethane or acetonitrile solvent.

Variation of the concentration of these common protic acids still resulted in a mixture of polymeric reaction products, but altered the rate. Polymerisation occurred with all concentrations of these mineral acid catalysts studied, except at exceedingly low catalyst concentrations where no reaction occurred over the time scale studied. Elevation of the reaction temperature eventually led to ring-opened products in all cases. These catalysts functioned well as redistribution catalysts, but did not work for the interconversion reaction. These protic acids (H_2SO_4, HCl, and HNO_3) provided a nucleophile strong enough to attack the silicon atom and open the ring under the conditions attempted. In summary, interconversion without by-products was not observed with these catalysts, suggesting that in these cases the reaction rates between redistribution/polymerisation and interconversion are similar, or that interconversion does not occur.

2.3 Nucleophiles for Cyclosiloxane Interconversion

Protic acids that provide a weakly nucleophilic conjugate base were also evaluated as catalysts for the interconversion of the 2,6-isomer. A weak nucleophile is postulated to coordinate with the silicon atom of a protonated cyclosiloxane, but not necessarily break the Si–O bond. This coordination forms a pentacoordinated silicon species. Pentacoordinated silicon species are capable of Berry pseudorotation about the silicon atom, as discussed in Section 1.5.[98] A series of pseudorotations about silicon could result in conversion of one stereoisomer to the other. This is a possible explanation for interconversion of the 2,6-isomers without producing the 2,4-isomers or other expected ring-opened products, but supporting data must be provided. Much of the following work is dedicated to exploring this hypothesis.

2.3.1 Evaluation of Methanesulphonic Acid Catalysed Interconversion

The interconversion reaction was attempted with 2,6-*cis* in the polar aprotic solvent nitromethane (CH_3NO_2), catalysed by methanesulphonic acid in order to determine the order of the reaction according to $J = k\,[2,6\text{-}cis]^x\,[\text{catalyst}]^y$. The conversion from 2,6-*cis* to an equimolar mixture of the 2,6-*cis* and 2,6-*trans* cyclosiloxane isomers was followed using the same GC method outlined for the triflic acid catalysed reactions (Section 2.1.1), again using naphthalene as the internal standard. According to first-order kinetics, a plot of ln [reactant] versus time produces a straight line whose slope represents the negative rate constant (-*k*). This is shown in Figure 2.18 for the interconversion of 20 mM 2,6-*cis* catalysed by 19 mM methanesulphonic acid in nitromethane solvent at 40°C. Good linearity is shown by a best-fit correlation ($R^2 = 0.999$).

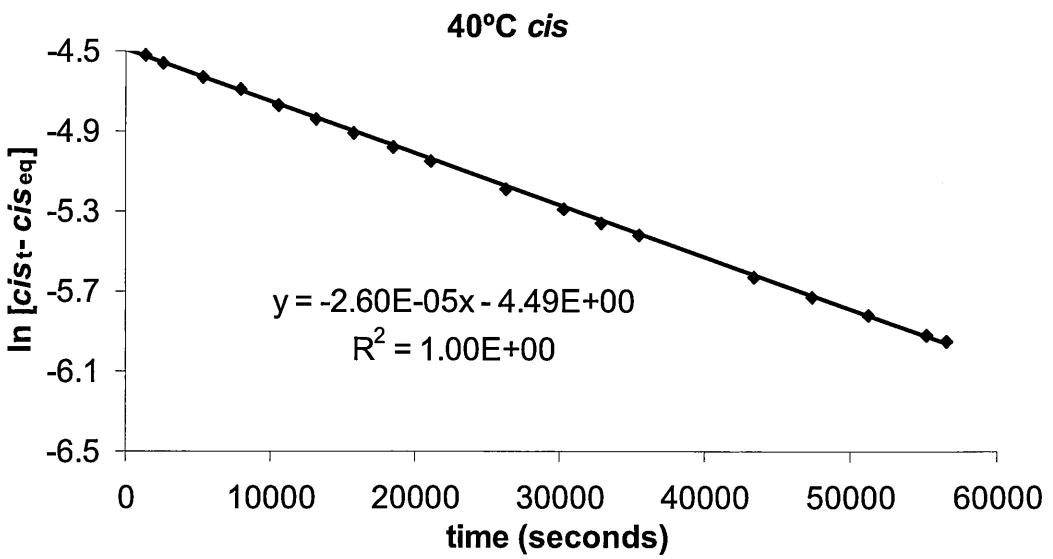


Figure 2.18 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 40°C according to first-order kinetic law, where GC data show the loss of the [2,6-*cis*] isomer

The reaction can be monitored by tracking either the loss of the 2,6-*cis* isomer reactant or the production of 2,6-*trans*. If no other products are formed, the rate of 2,6-*cis* loss and 2,6-*trans* production should be equivalent. This can be validated with an internal standard

method that accounts for mass balance. The rate constant at which 2,6-*cis* is lost (2.60 x 10^{-5} s^{-1}, from the slope in Figure 2.18) does equate to that obtained from the production of the 2,6-*trans* isomer (2.58 x 10^{-5} s^{-1}, in Figure 2.19) within experimental error.

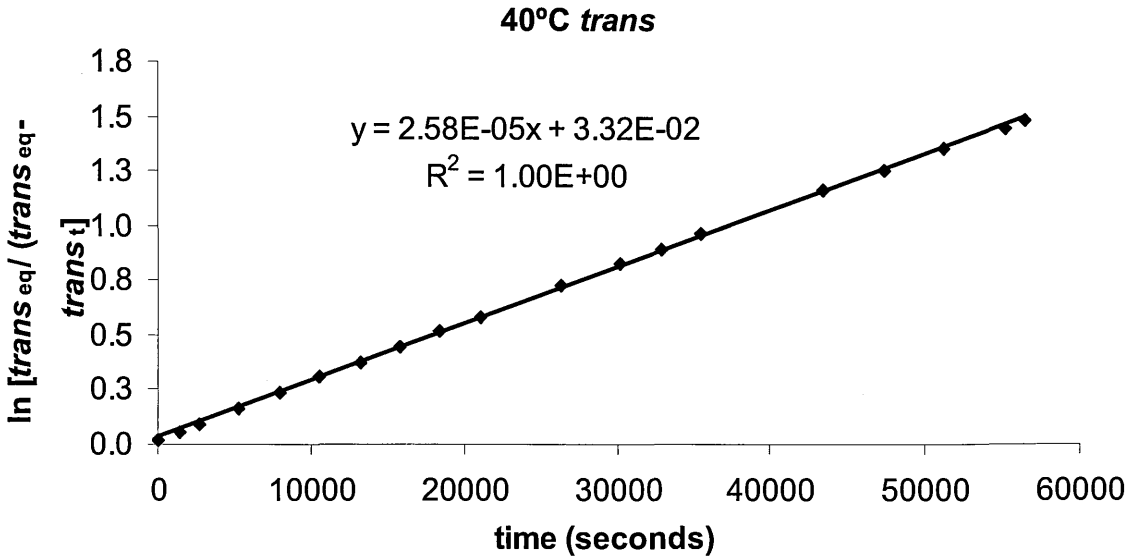


Figure 2.19 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 40°C according to first-order kinetic law, where GC data show the production of the [2,6-*trans*] isomer

The excellent linearity (R^2 = 0.999) of the above two representations of this methanesulphonic acid catalysed reaction suggests that this interconversion is first-order in 2,6-*cis* starting material. Thus, $x = 1$ for the order in 2,6-*cis* starting material according to $J = k\,[2,6\text{-}cis]^x\,[\text{catalyst}]^y$. First-order kinetic calculations in the cyclosiloxane starting material were applied to the results from this protic acid, as will be shown for the triflic acid catalysed reactions.

The reaction was evaluated over a range of catalyst concentrations while varying the temperature from 40 to 70°C in order to obtain the activation energy, Arrhenius constant, entropy, and enthalpy of reaction. The results of these experiments are documented in Appendix B, along with the plots based on the first-order kinetics law. The

rate constants calculated from these data over the 40 to 70°C range for methanesulphonic acid are summarised in Table 2.8.

	$[CH_3SO_3H]$ (M)	*k* (1/sec) (production of 2,6-*trans*)	*k* (1/sec) (-loss of 2,6-*cis*)
40°C			
13-1	2.35E-02	3.60E-05	3.64E-05
13-2	2.30E-02	2.76E-05	2.80E-05
13-3	2.12E-02	3.16E-05	3.19E-05
14-1	1.89E-02	2.58E-05	2.60E-05
14-2	2.58E-02	6.84E-05	6.93E-05
50°C			
11-1	2.32E-02	4.38E-05	4.45E-05
11-2	2.11E-02	2.92E-05	2.98E-05
11-3	2.35E-02	4.60E-05	4.67E-05
12-1	2.60E-02	7.15E-05	7.17E-05
12-2	1.89E-02	3.25E-05	3.30E-05
12-3	1.57E-02	2.14E-05	2.17E-05
60°C			
8-1	2.35E-02	6.03E-05	6.17E-05
8-2	1.89E-02	3.36E-05	3.43E-05
8-3	2.83E-02	9.27E-05	9.48E-05
9-1	2.14E-02	4.56E-05	4.64E-05
9-2	1.65E-02	2.40E-05	2.47E-05
9-3	1.41E-02	1.51E-05	1.54E-05
9-4	1.18E-02	9.75E-06	9.90E-06
10-1	2.57E-02	6.74E-05	6.86E-05
70°C			
5-1	3.53E-02	1.97E-04	1.99E-04
5-2	2.37E-02	7.47E-05	7.68E-05
5-3	1.19E-02	1.40E-05	1.45E-05
6-1	1.89E-02	3.95E-05	4.07E-05
6-2	1.67E-02	2.89E-05	2.99E-05
6-3	1.44E-02	2.08E-05	2.15E-05
7-1	2.13E-02	5.36E-05	5.57E-05
7-2	2.61E-02	8.71E-05	9.04E-05
7-3	2.82E-02	1.07E-04	1.11E-04

Table 2.8 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of methanesulphonic acid in nitromethane at 40 to 70°C

The methanesulphonic acid catalysed interconversion reactions above and the experiments catalysed by triflic acid (Table 2.13) were treated with a similar concentration

(20 mM) of 2,6-*cis* starting material, in nitromethane solvent. Very different catalytic activity towards interconversion is obtained with these two catalysts. For example, a rate constant of 2.64 x 10^{-5} s^{-1} (Sample 148-3) was obtained with 0.80 mM triflic acid, while 18.9 mM of methanesulphonic acid was necessary to impart a similar rate constant of 2.58 x 10^{-5} s^{-1} (Sample 14-1) for interconversion, at 40°C. Thus, greater than twenty times more methanesulphonic acid than triflic acid resulted in a similar rate constant of interconversion.

In order to determine the order in catalyst, the rate constants (Table 2.8) were plotted against the [acid] used. Figure 2.20 shows this for the 60°C data following the loss of the 2,6-*cis* starting material as an example.

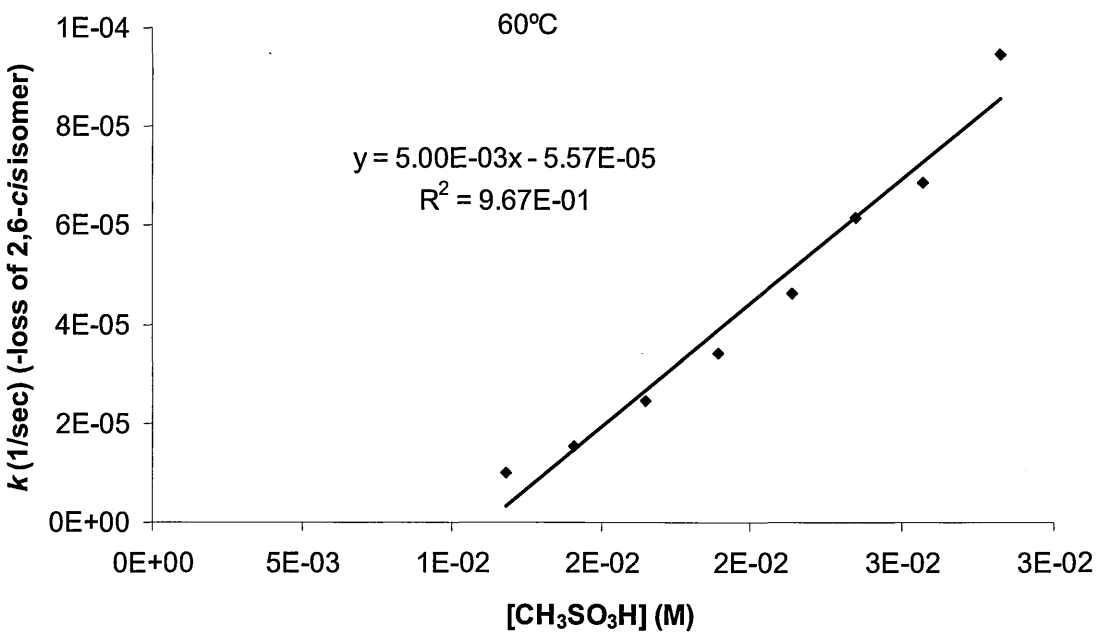


Figure 2.20 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of methanesulphonic acid in nitromethane at 60°C

If a first-order fit to the data is imposed, 12 mM methanesulphonic acid is calculated to be inactive catalyst (*x*-axis intercept) at 60°C. The curvature in the 60°C data

(Figure 2.20), however, is an indication that this interconversion reaction is not simply first-order in catalyst. The concentrations of inactive catalyst determined from the linear fit of these data are, of course, not accurate in regions where first-order kinetics does not apply. A similar trend is observed when comparing the methanesulphonic acid data over the 40 to 70°C temperature range studied (Figure 2.21).

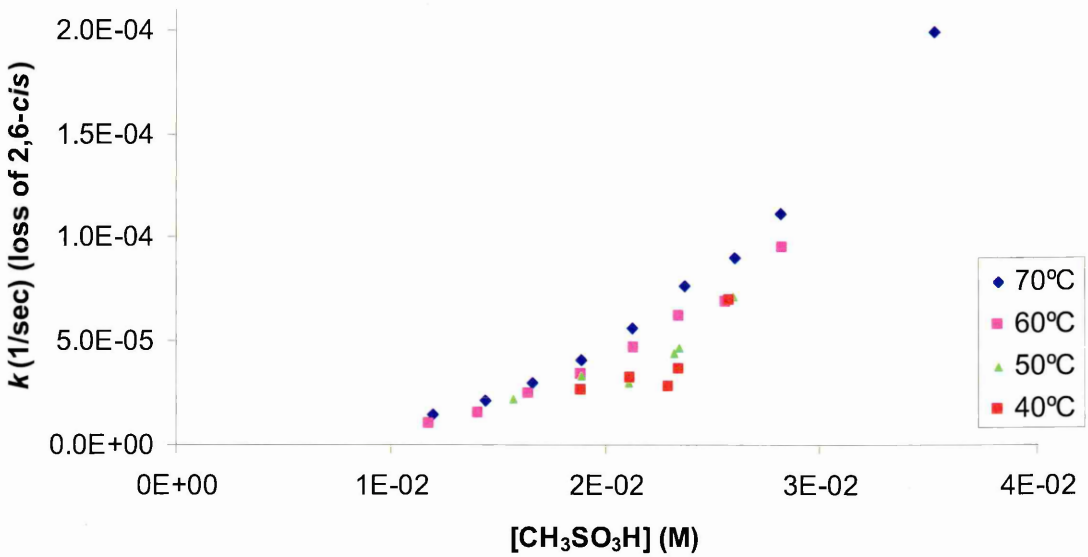


Figure 2.21 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of methanesulphonic acid in nitromethane at 40 to 70°C

The curvature observed (Figure 2.21) again highlights that the interconversion reaction is not accurately depicted by a linear extrapolation and is not first-order in catalyst. Second-order kinetics best describe this reaction, and a binomial fit is shown in Figure 2.22.

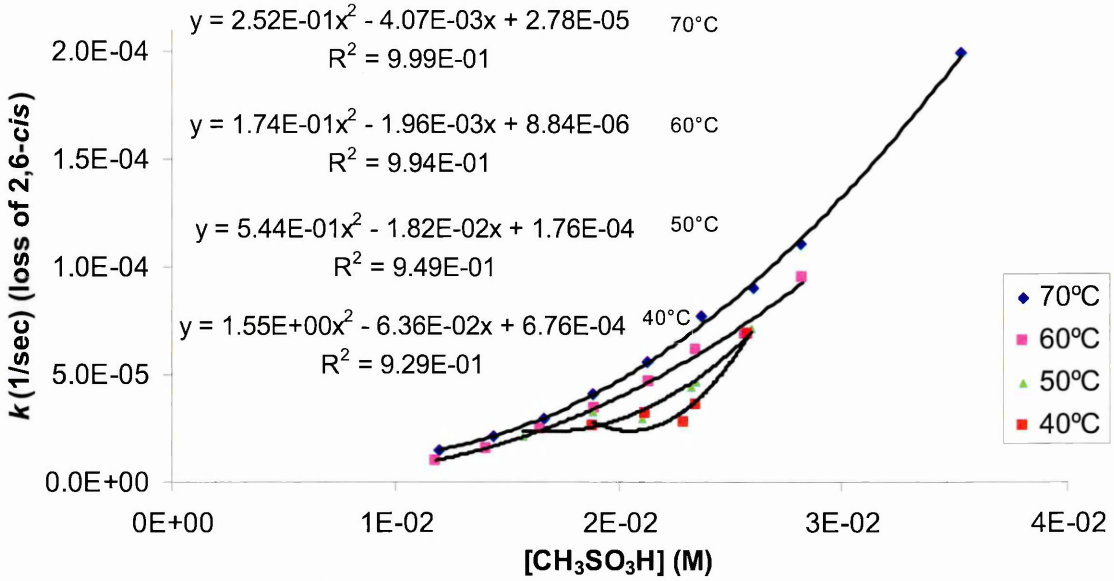


Figure 2.22 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of methanesulphonic acid in nitromethane at 40 to 70°C, with a binomial fit line shown.

A correction of 0.0025 M provides the best fit for the curves of a second-order reaction in methanesulphonic acid. The corrected acid concentrations and corresponding rate constants are shown in Table 2.9.

	$[CH_3SO_3H]$ (M)	$[CH_3SO_3H]$ (M) (corrected)	*k* (1/sec) (-loss of 2,6-*cis*)	ln $[CH_3SO_3H]$ (corrected)	ln *k* (-loss of 2,6-*cis*)
40°C					
13-1	2.35E-02	2.10E-02	3.64E-05	-3.86	-10.22
13-2	2.30E-02	2.05E-02	2.80E-05	-3.89	-10.48
13-3	2.12E-02	1.87E-02	3.19E-05	-3.98	-10.35
14-1	1.89E-02	1.64E-02	2.60E-05	-4.11	-10.56
14-2	2.58E-02	2.33E-02	6.93E-05	-3.76	-9.58
50°C					
11-1	2.32E-02	2.07E-02	4.45E-05	-3.88	-10.02
11-2	2.11E-02	1.86E-02	2.98E-05	-3.99	-10.42
11-3	2.35E-02	2.10E-02	4.67E-05	-3.86	-9.97
12-1	2.60E-02	2.35E-02	7.17E-05	-3.75	-9.54
12-2	1.89E-02	1.64E-02	3.30E-05	-4.11	-10.32
12-3	1.57E-02	1.32E-02	2.17E-05	-4.32	-10.74
60°C					
8-1	2.35E-02	2.10E-02	6.17E-05	-3.86	-9.69
8-2	1.89E-02	1.64E-02	3.43E-05	-4.11	-10.28
8-3	2.83E-02	2.58E-02	9.48E-05	-3.66	-9.26
9-1	2.14E-02	1.89E-02	4.64E-05	-3.97	-9.98
9-2	1.65E-02	1.40E-02	2.47E-05	-4.27	-10.61
9-3	1.41E-02	1.16E-02	1.54E-05	-4.46	-11.08
9-4	1.18E-02	9.30E-03	9.90E-06	-4.68	-11.52
10-1	2.57E-02	2.32E-02	6.86E-05	-3.76	-9.59
70°C					
5-1	3.53E-02	3.28E-02	1.99E-04	-3.42	-8.52
5-2	2.37E-02	2.12E-02	7.68E-05	-3.85	-9.47
5-3	1.19E-02	9.44E-03	1.45E-05	-4.66	-11.14
6-1	1.89E-02	1.64E-02	4.07E-05	-4.11	-10.11
6-2	1.67E-02	1.42E-02	2.99E-05	-4.26	-10.42
6-3	1.44E-02	1.19E-02	2.15E-05	-4.43	-10.75
7-1	2.13E-02	1.88E-02	5.57E-05	-3.98	-9.80
7-2	2.61E-02	2.36E-02	9.04E-05	-3.75	-9.31
7-3	2.82E-02	2.57E-02	1.11E-04	-3.66	-9.11

Table 2.9 Interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of methanesulphonic acid in nitromethane at 40 to 70°C

The rate constant data (Table 2.9) were used to determine the order of the reaction in catalyst. The slope of the best-fit line of the logarithm of the concentration of the catalyst concentration versus the logarithm of the rate constant should equate to the order in catalyst. The results for the interconversion of 2,6-*cis* catalysed by methanesulphonic acid over the 40 to 70°C temperature range are contained in Figure 2.23.

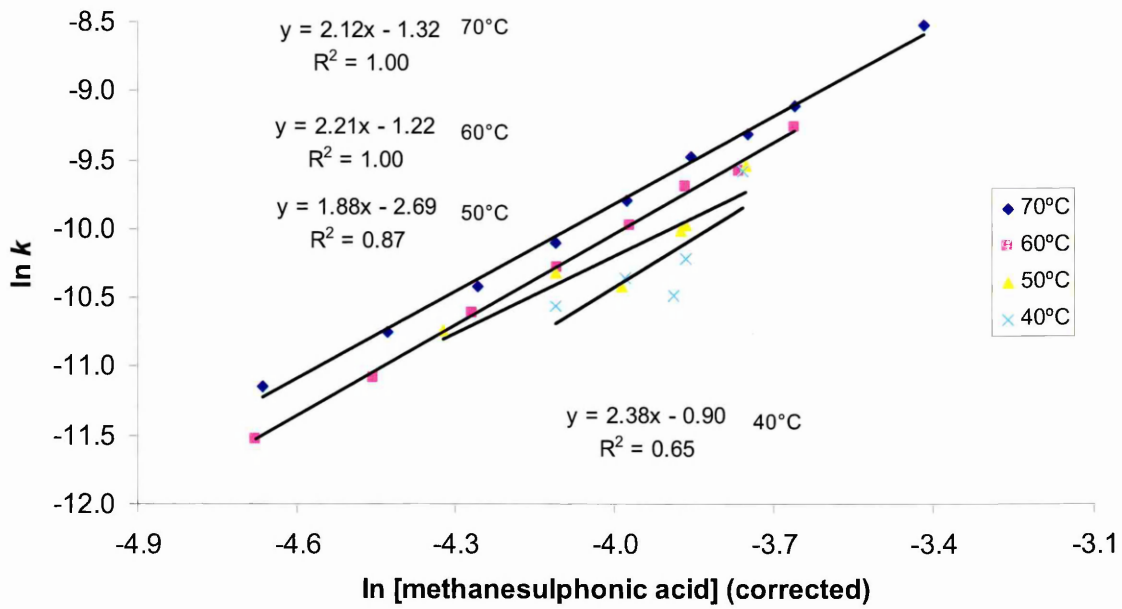


Figure 2.23 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of methanesulphonic acid (corrected) in nitromethane at 40 to 70°C

The order of the reaction with respect to methanesulphonic acid catalyst is 1.9 to 2.4 over a 40 to 70°C temperature range. Overall, the linear fit of these data is not as good as expected. This is partly due to the polymerisation reactions that occurred with the cyclosiloxane when catalysed by methanesulphonic acid, especially observed at the higher temperatures, where the sum of the concentrations of 2,6-*cis* and 2,6-*trans* decreased. A large concentration of methanesulphonic acid was used for these interconversion reactions to obtain reasonable reaction rates of interconversion. This larger concentration of catalyst appears to cause other complications, mostly polymerisation. The polymerisation observed with this acid is discussed further in Section 2.3.1.1.

The order of the reaction with respect to methanesulphonic acid is not 1 and is most likely closer to 2 determined from data shown in Figure 2.23. The order in the methanesulphonic acid catalysed interconversion reaction is $y = 2$, according to $J = k$ [2,6-*cis*]^x [catalyst]^y, and $x = 1$ for the order in 2,6-*cis* starting material. Second order in

catalyst suggests two molecules of catalyst participate in the rate determining step of the reaction. Each methanesulphonic acid molecule provides both a proton and a nucleophile. The methanesulphonate anion is considered the strongest nucleophile in the system—stronger than nitromethane, and stronger than water. This may lead to both H^+ and $(CH_3SO_3)^-$ being involved in the rate determining step of the mechanism. Protonation of the oxygen followed by nucleophilic attack on the adjacent silicon are common reaction pathways in siloxane mechanisms. A pentacoordinate intermediate is proposed in Figure 2.24 which accounts for the rate equation: $J = k\,[2,6\text{-}cis]^1\,[\text{catalyst}]^2$ or, more precisely, $J = k\,[2,6\text{-}cis]^1\,[H^+]^1[CH_3SO_3^-]^1$.

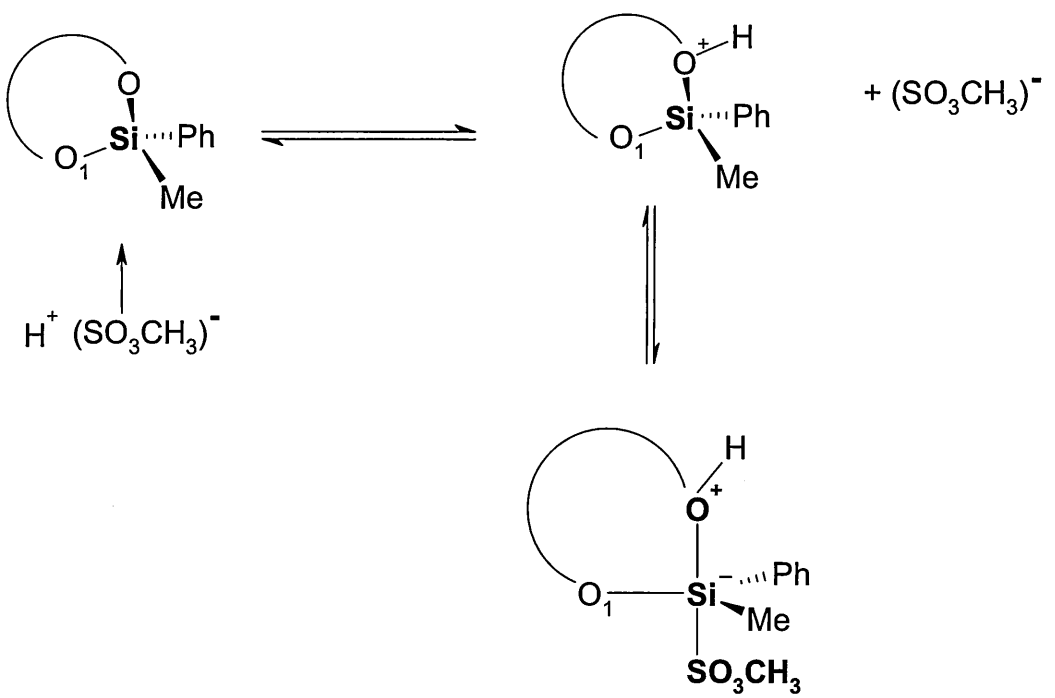


Figure 2.24 Proposed initial steps of interconversion for 2,6-*cis* in a polar aprotic solvent catalysed by methanesulphonic acid

The catalyst and the reactant concentrations were held constant, while varying the temperature from 40 to 70°C in order to obtain the activation energy, Arrhenius constant, entropy, and enthalpy of reaction. A negative entropy would support a more ordered

transition state. The resulting rate constant data and the corresponding temperature data are displayed in Table 2.10 for the interconversion reaction catalysed by methanesulphonic acid, based on the loss of 2,6-*cis* data.

	$[CH_3SO_3H]$ (M) (corrected)	k (sec^{-1}) (-loss of 2,6-cis)	ln $[CH_3SO_3H]$ (corrected)	$k/[CH_3SO_3H]^2$ (sec^{-1}/M)	ln ($k/[CH_3SO_3H]^2$)
40°C					
13-1	2.10E-02	3.64E-05	-3.86	8.27E-02	-2.49
13-2	2.05E-02	2.80E-05	-3.89	6.69E-02	-2.70
13-3	1.87E-02	3.19E-05	-3.98	9.14E-02	-2.39
14-1	1.64E-02	2.60E-05	-4.11	9.71E-02	-2.33
14-2	2.33E-02	6.93E-05	-3.76	1.28E-01	-2.06
Ave.				*9.31E-02*	*-2.37*
Std. Dev.					*1.63E-01*
50°C					
11-1	2.07E-02	4.45E-05	-3.88	1.03E-01	-2.27
11-2	1.86E-02	2.98E-05	-3.99	8.63E-02	-2.45
11-3	2.10E-02	4.67E-05	-3.86	1.06E-01	-2.24
12-1	2.35E-02	7.17E-05	-3.75	1.30E-01	-2.04
12-2	1.64E-02	3.30E-05	-4.11	1.23E-01	-2.10
12-3	1.32E-02	2.17E-05	-4.32	1.24E-01	-2.09
Ave.				*1.12E-01*	*-2.19*
Std. Dev.					*1.61E-01*
60°C					
8-1	2.10E-02	6.17E-05	-3.86	1.40E-01	-1.96
8-2	1.64E-02	3.43E-05	-4.11	1.27E-01	-2.06
8-3	2.58E-02	9.48E-05	-3.66	1.43E-01	-1.95
9-1	1.89E-02	4.64E-05	-3.97	1.30E-01	-2.04
9-2	1.40E-02	2.47E-05	-4.27	1.26E-01	-2.07
9-3	1.16E-02	1.54E-05	-4.46	1.14E-01	-2.17
9-4	9.30E-03	9.90E-06	-4.68	1.14E-01	-2.17
10-1	2.32E-02	6.86E-05	-3.76	1.27E-01	-2.06
Ave.				*1.28E-01*	*-2.06*
Std. Dev.					*8.16E-02*
70°C					
5-1	3.28E-02	1.99E-04	-3.42	1.85E-01	-1.69
5-2	2.12E-02	7.68E-05	-3.85	1.71E-01	-1.76
5-3	9.44E-03	1.45E-05	-4.66	1.63E-01	-1.82
6-1	1.64E-02	4.07E-05	-4.11	1.51E-01	-1.89
6-2	1.42E-02	2.99E-05	-4.26	1.49E-01	-1.90
6-3	1.19E-02	2.15E-05	-4.43	1.51E-01	-1.89
7-1	1.88E-02	5.57E-05	-3.98	1.58E-01	-1.84
7-2	2.36E-02	9.04E-05	-3.75	1.62E-01	-1.82
7-3	2.57E-02	1.11E-04	-3.66	1.68E-01	-1.78
Ave.				*1.62E-01*	*-1.82*
Std. Dev.					*6.99E-02*

Table 2.10 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of methanesulphonic acid in nitromethane at 40 to 70°C

The Arrhenius plot (Figure 2.25) for the interconversion reaction catalysed by

methanesulphonic acid was used to obtain the activation energy as well as the Arrhenius constants.

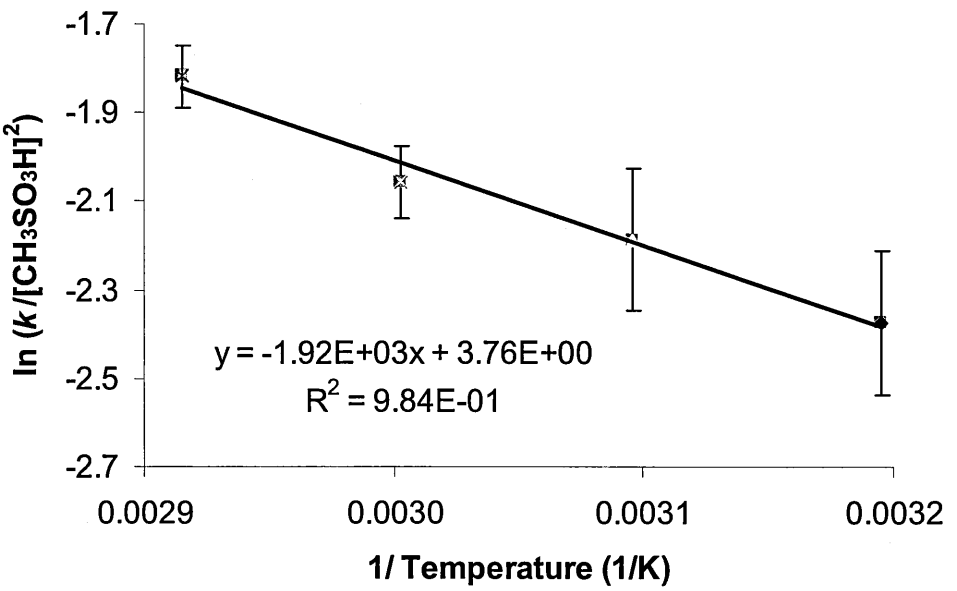


Figure 2.25 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by methanesulphonic acid in nitromethane at 40 to 70°C

The activation energy for the interconversion reaction based on the loss of 2,6-*cis* is (slope x 8.314 J/mol K) = 16.0 kJ/mol ± 3.6 % with methanesulphonic acid. The Arrhenius constant was calculated from the same data as ($e^{3.76}$) = 42.9 ± 3.6 % for methanesulphonic acid. These small Arrhenius constants imply a highly oriented transition state for the interconversion reaction. The difference in values is due to the method used to obtain the Arrhenius constants, which has an inherently high error because of the extrapolation necessary to obtain these values for the Arrhenius constant. The actual data reside a long way from the intercept and thus a small error in the data and thus the slope drastically affects the *y*-intercept value.

An Eyring plot was used to obtain values for entropy and enthalpy of activation for this interconversion reaction catalysed by methanesulphonic acid. This is the same

transformation that was performed on the triflic acid results and is shown in Figure 2.26 for the interconversion reaction catalysed by methanesulphonic acid.

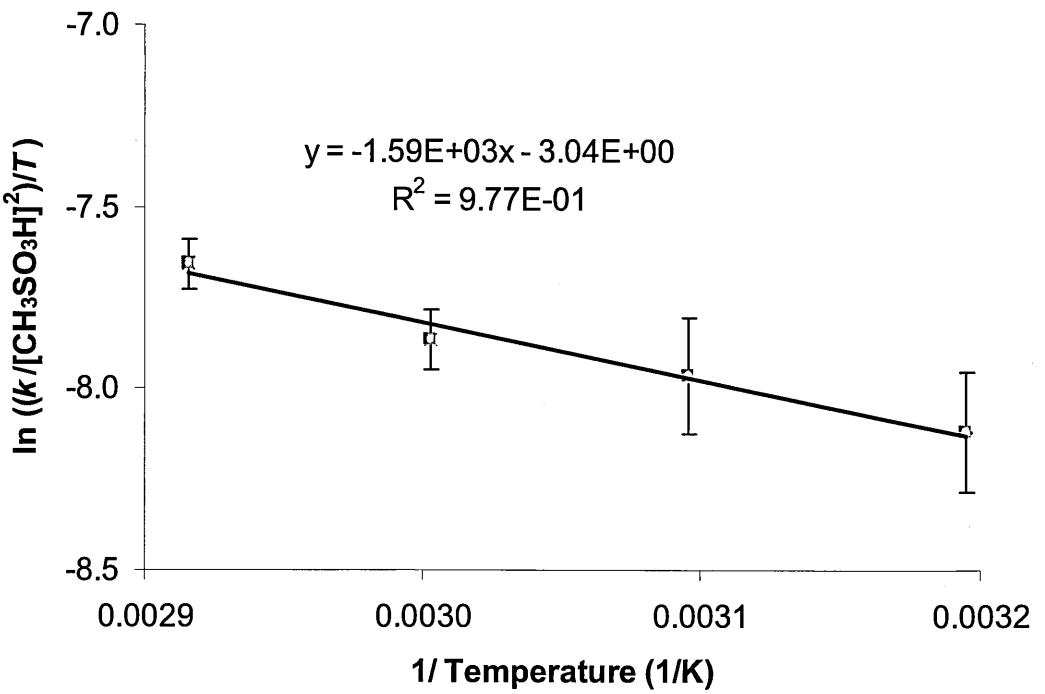


Figure 2.26 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 23.5 mM methanesulphonic acid in nitromethane at 40 to 70°C

From Figure 2.26 the entropy of activation $\Delta S^{\ddagger}$ = 8.314 J/mol K (intercept – 23.76), and the enthalpy of activation $\Delta H^{\ddagger}$ = -slope x R.

	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
	(8.314 J/mol K x slope)	***R* x (intercept–23.76)**
CH_3SO_3H	13.2 kJ/mol ± 3.6%	–222 J/mol K ± 3.6%

A negative entropy was obtained, which supports an ordered transition state. This is consistent with the proposed pentacoordinate intermediate. Pseudorotation of a pentacoordinate silicon intermediate mechanistically supports interconversion products, a negative entropy, and the rate equation: $J = k$ [2,6-*cis*]^1 [catalyst]^2.

A larger number of pentacoordinate silicon complexes are known relative to

carbon.[97] Hypervalent (more than four bonds to silicon) silicon compounds generally contain halogen, nitrogen, or oxygen ligands around the silicon. The predominant stereochemistry for pentacoordinate silicon is trigonal bipyramidal. Voronkov et al. showed that 1-chlorosilatrane (Figure 2.27) exhibits trigonal bipyramidal geometry with a 2.02Å Si-N bond length and a 2.15Å Si-Cl bond length.[111]

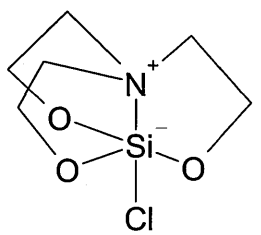


Figure 2.27 Pentacoordinated 1-chlorosilatrane compound

The chlorine and nitrogen leaving groups are located in the axial positions.

The mechanisms for 2,6-isomer interconversion, suggested by Frye and Spielvogel, involving the siloxane bond breaking and re-cyclising to produce only the 2,6-stereoisomers, without production of any linear species, appears extraordinary for this interconversion reaction. A proposed alternative mechanism proceeds through a pentacoordinate silicon species that undergoes pseudorotation of the ligands around silicon (Figure 2.24).

The nucleophile attacks the silicon to form a pentacoordinate intermediate. A backside attack would cause inversion of configuration about the silicon atom if there were a good leaving group in the opposite axial position to the nucleophile. At this point, the breaking of the silicon to protonated oxygen bond would provide a mechanistic pathway for the ring-opening polymerisation. The formed silanol polymerises through condensation, which is enhanced by solvation of a polar solvent. This bond breaking leads to polymerisation and does not support a ring-opening interconversion mechanism, unless intramolecular ring closure is faster than polymerisation.

If the nucleophile and the leaving group on silicon were the same (e.g. methoxy) this would provide a path for the racemisation Sommer observed in methanol.[112] Under conditions of only interconversion of 2,6-*cis* this siloxane bond is not broken, otherwise polymerisation would ensue. Pseudorotation is suggested to account for interconversion without siloxane bond breaking.

Extra-coordinate siloxane species have been shown to exist and can be an important part of the mechanisms involving silicon, especially substitution.[113] The pentacoordinate silicon in trigonal bipyramidal form can internally exchange, or pseudorotate, its ligands as discussed in Section 1.5. This pseudorotation (or Berry-pseudorotation) moves two equatorial ligands of a pentacoordinate silicon in the trigonal bipyramid through a square pyramidal geometry to the axial positions in the final structure of Figure 2.28. Calculations by Dieters and Holmes support a pentacoordinate pseudorotation mechanism for nucleophilic substitution at silicon.[114, 115]

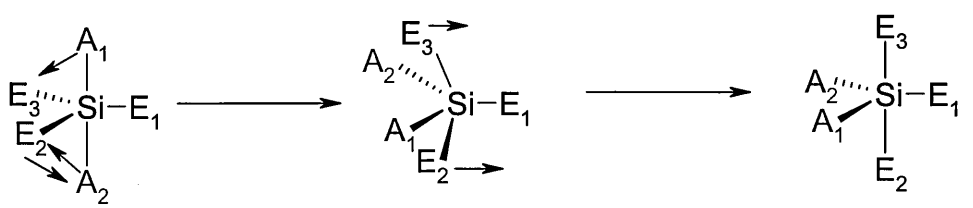
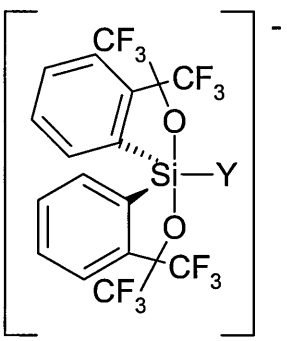


Figure 2.28 Pseudorotation of three equatorial (E) ligands and two axial (A) ligands around silicon

Pseudorotation appears to offer a route to convert one stereoisomer into the other (i.e. 2,6-*cis* → 2,6-*trans*). X-ray crystallographic data of pentacoordinate silicon complexes with geometries ranging from trigonal bipyramidal to square pyramidal were published by Holmes et al., which provides evidence of Berry's pseudorotation with silicon.[116]

Dieters and Holmes have shown that nucleophilic attack at the axial position is

lower energy than equatorial attack, and retention of stereochemistry is obtained by pseudorotation.[114, 115] Corriu reported the E_a for inversion of configuration about Si as 28.6 kcal/mol (119.7 kJ/mol) (Y = *n*-butyl), and decreasing to 16.8 kcal/mol (70.3 kJ/mol) for the more electronegative Y = CN analogue.[92]



Martin has shown the above molecule to invert through pseudorotation and not through the Corriu hexacoordinate species discussed below for Y=pyridine, $Bu_4N^+F^-$, $Ph_4N^+OH^-$, $C_6H_5^-Li^+$.[117, 118] Corriu et al. observed an activation energy $\Delta G^{\ddagger}$ of 9.4 kcal/mol for pseudorotation in the pentacoordinate compound in Figure 2.29.[119]

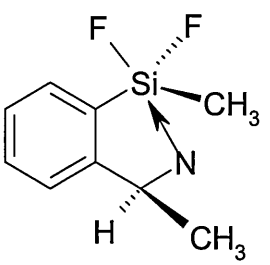


Figure 2.29 Pentacoordinate model compound.

A proposed pathway for the acid catalysed interconversion that involves a pentacoordinate intermediate followed by three consecutive pseudorotations is shown in Figure 2.30.

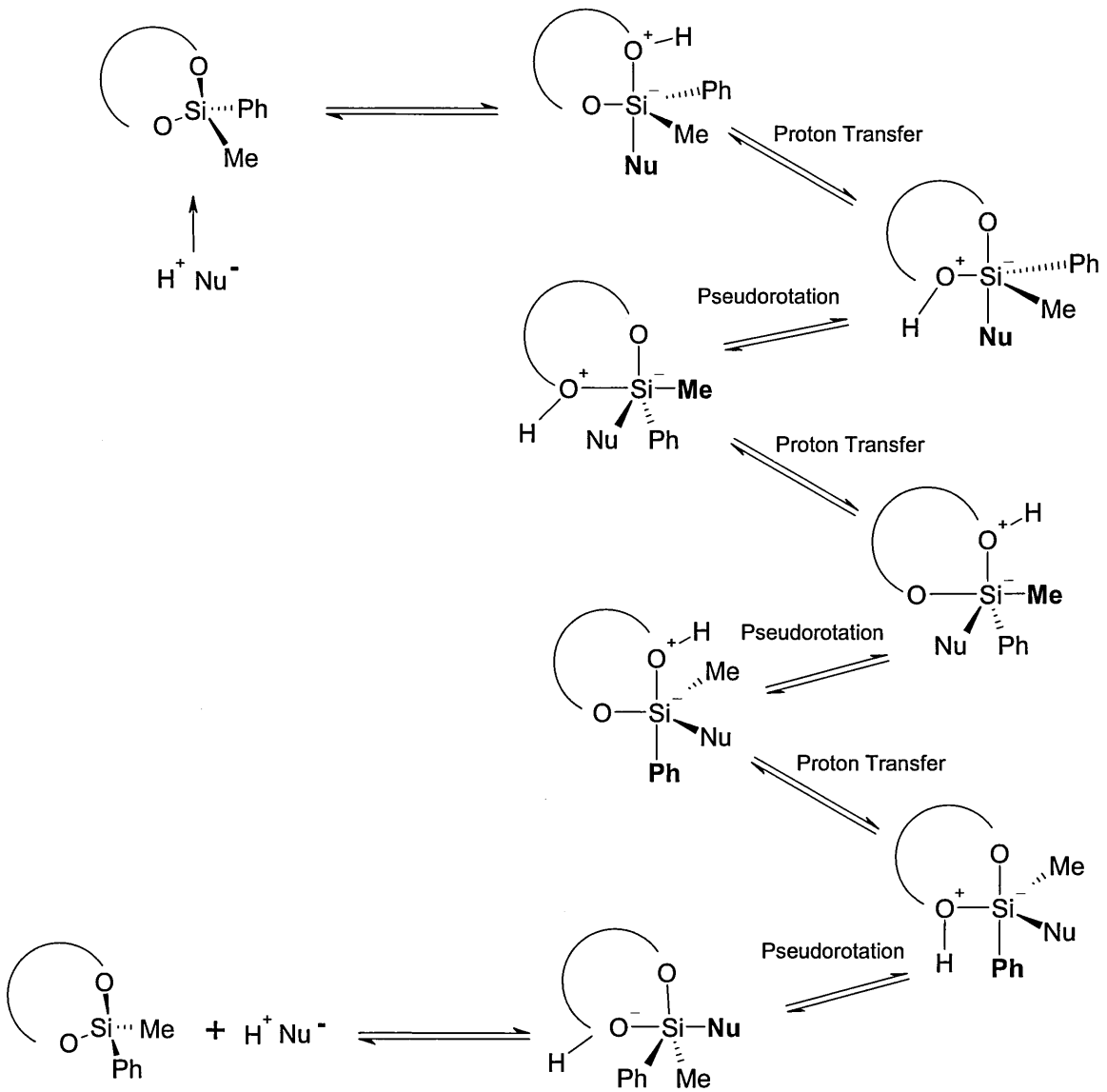


Figure 2.30 Proposed pseudorotation mechanism for interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane in a polar aprotic solvent

The proton transfers included in Figure 2.30 are suggested to occur as they reduce the energy barrier to pseudorotation.

The interconversion mechanism suggested above does not include siloxane bond breaking, but instead is similar to the pre-complex formation followed by pseudorotation suggested by Chang et al.[82] Chang et al. studied the interconversion of 2,4,6-*cis*-trimethyl-2,4,6-triphenylcyclotresiloxane catalysed by alkyl ammonium salts in DMSO. They suggest a hydrogen bond complex between the cation (e.g. n-$C_8H_{17}NH_3^+$) and the oxygen

in the cyclosiloxane ring, as well as a complex between the adjacent silicon atom and the BF_4^-. Approximately second order in catalyst was measured, which the authors use to explain the dual complexation of the catalyst in the ionic form with the cyclosiloxane. A negative value for $\Delta S^{\ddagger}$ (-0.29 cal/mol K) was measured, consistent with a more ordered transition state, similar to our 2,6-*cis* interconversion results. Chang et al. determined the rate constant for 5.37 x 10^{-3} M *n*-$C_8H_{17}NH_3^+BF_4^-$ catalysed interconversion as 1.04 x 10^{-2} min^{-1} (1.73 x 10^{-2} sec^{-1}) at 25°C.

2.3.1.1 Polymerisation

When compared to the interconversion at similar reaction rates catalysed by triflic acid, as will be shown in 2.3.2, the weaker acid of methanesulphonic acid produces relatively more ring-opened products. The major difference is that only 0.80 mM triflic acid catalyst was used to study the interconversion reaction, while at least 23 times more methanesulphonic acid (19 mM) was required at 40°C to achieve similar reaction rates. The interconversion of 2,6-*cis* to an approximate 50:50 equilibrium mixture of the stereoisomers 2,6-*cis* and 2,6-*trans* was followed either by observing the loss of the *cis* isomer or the production of the *trans* isomer in the GC data presented above. The concentration of the 2,6-*cis* isomer plus the concentration of the 2,6-*trans* isomer will remain constant when no other materials are being produced. When the sum of these isomers begins to decrease, reactions other than interconversion have occurred which are consuming either the starting material or the products or both. The products other than 2,6-*cis* and 2,6-*trans* are assumed to be the result of ring-opening and thus polymerisation. Also, as the reaction proceeds, increasing amounts of macrocyclics and oligomers are evident in the GC. So, the data gathered from the interconversion reaction of 2,6-*cis* catalysed by methanesulphonic acid was also used to quantify the amount of

polymerisation of these cyclosiloxanes that occurs. The [2,6-*cis*] + [2,6-*trans*] sum was used to determine the rate of polymerisation that occurs in the methanesulphonic acid catalysed, interconversion reaction discussed above. All of the data collected were used for these polymerisation analyses, not just the first 80% of interconversion reaction (at which point there is 60% 2,6-*cis* and 40% 2,6-*trans* remaining), which was used for the interconversion reaction and is typical with kinetic evaluations. This was done in order to study the polymerisation, which occurs more slowly than the interconversion and, therefore, becomes more evident after the interconversion is well underway, or is nearly complete. The slower polymerisation reaction, however, was not followed to completion because this analysis is focused on the interconversion reaction studied with the GC technique outlined above.

The rate constant for polymerisation was obtained by following the decrease of the sum of [2,6-*cis*] + [2,6-*trans*] versus time and analysing the data for first-order kinetics. The results from the loss of 2,6-*cis* and 2,6-*trans* catalysed by 23.5 mM methanesulphonic acid (Sample 5-1) at 40°C are plotted (Figure 2.31) to provide the rate constant of polymerisation.

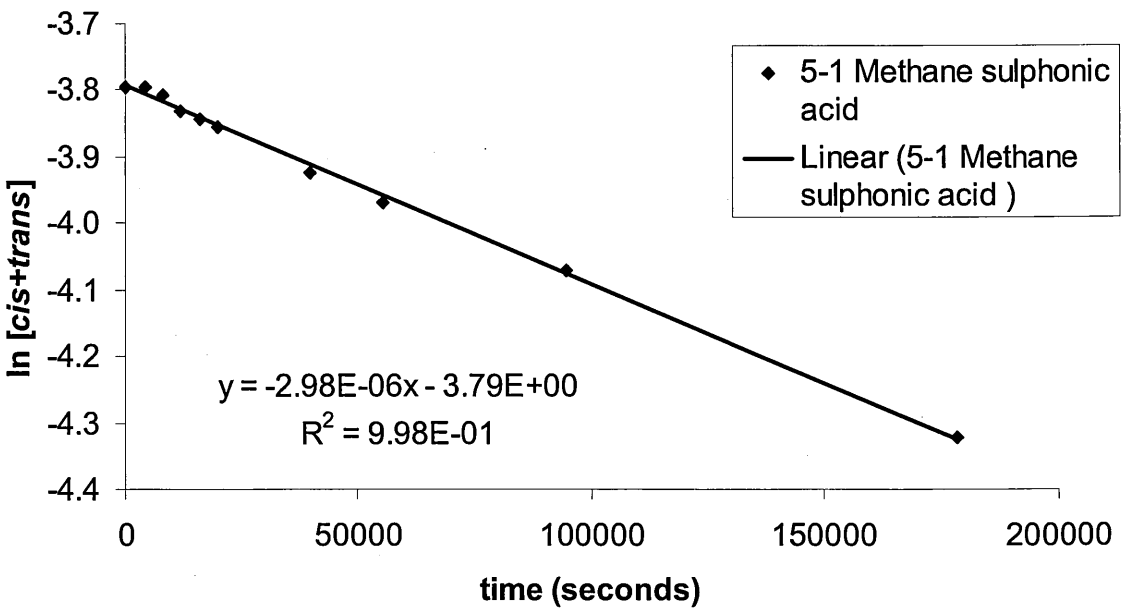


Figure 2.31 Polymerisation of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by methanesulphonic acid in nitromethane at 40°C

Good linearity of the data to the best-fit line is observed (Figure 2.31), showing that the polymerisation is first-order in starting material. The order in 2,6-*cis* starting material is $x = 1$ according to $J = k\,[2,6\text{-}cis]^x\,[\text{catalyst}]^y$. The remaining methanesulphonic acid catalysed polymerisation data were evaluated according to the first-order kinetic law. The rate constants for each of these samples were calculated from the slope of the first-order graphs contained in Appendix B. Table 2.11 contains these rate constants for polymerisation with methanesulphonic acid at various temperatures and catalyst concentrations. The catalyst concentrations were corrected by 0.0025 M, just as was performed with the methanesulphonic acid catalysed interconversion data.

	$[CH_3SO_3H]$ (M)	corrected [acid] (M)	*k* (*cis+trans*) (1/sec)	ln $[CH_3SO_3H]$ (corrected)	ln *k*
40°C					
13-1	2.35E-02	2.10E-02	3.97E-07	-3.86	-14.7
13-2	2.30E-02	2.05E-02	3.21E-07	-3.89	-15.0
13-3	2.12E-02	1.87E-02	2.80E-07	-3.98	-15.1
14-1	1.89E-02	1.64E-02	1.99E-07	-4.11	-15.4
14-2	2.58E-02	2.33E-02	9.47E-07	-3.76	-13.9
50°C					
11-1	2.32E-02	2.07E-02	5.67E-07	-3.88	-14.4
11-2	2.11E-02	1.86E-02	4.61E-07	-3.99	-14.6
11-3	2.35E-02	2.10E-02	4.83E-07	-3.86	-14.5
12-1	2.60E-02	2.35E-02	8.09E-07	-3.75	-14.0
12-2	1.89E-02	1.64E-02	4.93E-07	-4.11	-14.5
12-3	1.57E-02	1.32E-02	3.42E-07	-4.32	-14.9
60°C					
8-1	2.35E-02	2.10E-02	7.73E-07	-3.86	-14.1
8-2	1.89E-02	1.64E-02	5.91E-07	-4.11	-14.3
8-3	2.83E-02	2.58E-02	1.44E-06	-3.66	-13.4
9-1	2.14E-02	1.89E-02	7.91E-07	-3.97	-14.1
9-2	1.65E-02	1.40E-02	5.15E-07	-4.27	-14.5
9-3	1.41E-02	1.16E-02	2.65E-07	-4.46	-15.1
9-4	1.18E-02	9.30E-03	1.68E-07	-4.68	-15.6
10-1	2.57E-02	2.32E-02	1.15E-06	-3.76	-13.7
70°C					
5-1	3.53E-02	3.28E-02	2.98E-06	-3.42	-12.7
5-2	2.37E-02	2.12E-02	1.67E-06	-3.85	-13.3
5-3	1.19E-02	9.44E-03	4.64E-07	-4.66	-14.6
6-1	1.89E-02	1.64E-02	1.02E-06	-4.11	-13.8
6-2	1.67E-02	1.42E-02	9.07E-07	-4.26	-13.9
6-3	1.44E-02	1.19E-02	7.63E-07	-4.43	-14.1
7-1	2.13E-02	1.88E-02	1.34E-06	-3.98	-13.5
7-2	2.61E-02	2.36E-02	1.98E-06	-3.75	-13.1
7-3	2.82E-02	2.57E-02	4.10E-06	-3.66	-12.4

Table 2.11 Polymerisation data for 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of methanesulphonic acid in nitromethane at 40 to 70°C.

The data from Table 2.11 can be used to determine the order in catalyst for the polymerisation by comparing the log of the concentration of the corrected catalyst concentration versus the log of the rate constant. The slope of the line (Figure 2.32) indicates the order to be 1.4 to 4.6 for the polymerisation catalysed by methanesulphonic acid over the 40 to 70°C temperature range.

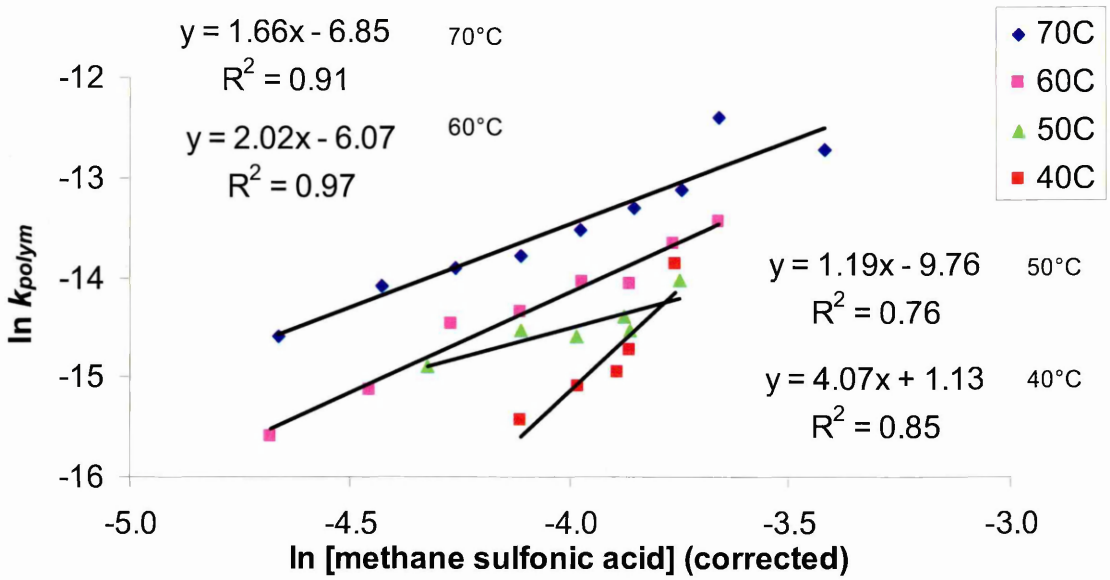


Figure 2.32 Polymerisation of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of methanesulphonic acid in nitromethane at 40 to 70°C.

The results (Figure 2.32) do not support first-order kinetics for the catalyst over the temperature range studied. The results shown in the graph predict an order of 1.2 to 2.0 for the data obtained over 50 to 70°C, while the 40°C results predict an order of 4.1 in catalyst, but the fit is poor at the lower temperatures.

There are several complications that can be expected from the analysis of these data. Only a small amount of polymerisation occurred at lower temperatures, resulting in a limited number of data points, therefore small errors distorted the results significantly. Only a small amount of polymerisation was observed under these catalyst concentrations at 40°C. Therefore, the 40°C data are useful for interconversion results, but not as useful for the study of polymerisation. Polymerisation occurred rapidly at higher temperatures, which quickly led to polymers of a large MW that could not be detected by the GC. The data sets are incomplete because at some point the polymers were too large to elute from the GC column. This was not an issue initially, as our study followed the loss of the starting material, but eventually the reaction mixture clogged the syringe as well, resulting

in a significant drop in the sum of [2,6-*cis*] + [2,6-*trans*], although the internal standard method should account for this. This only reinforces that this GC technique is not ideal for the study of polymerisation, and the following polymerisation analyses only provide an indication of the kinetics. The results in Figure 2.32 are an indication that this reaction is not simple first-order in catalyst. These polymerisation kinetic results are similar to what was observed for the interconversion reactions catalysed by methanesulphonic acid (i.e. first-order in 2,6-*cis* starting material, and complex order in catalyst).

The order for polymerisation with respect to methanesulphonic acid catalyst is approximately second order when more than trace polymerisation occurs (60 and 70°C data). This is similar to the interconversion results, and second order in catalyst may again suggest H^+ and $(CH_3SO_3)^-$ are both involved in the rate determining step of the mechanism. A common pentacoordinate silicon intermediate can be proposed for both the interconversion and the polymerisation of 2,6-*cis* catalysed by methanesulphonic acid (Figure 2.33).

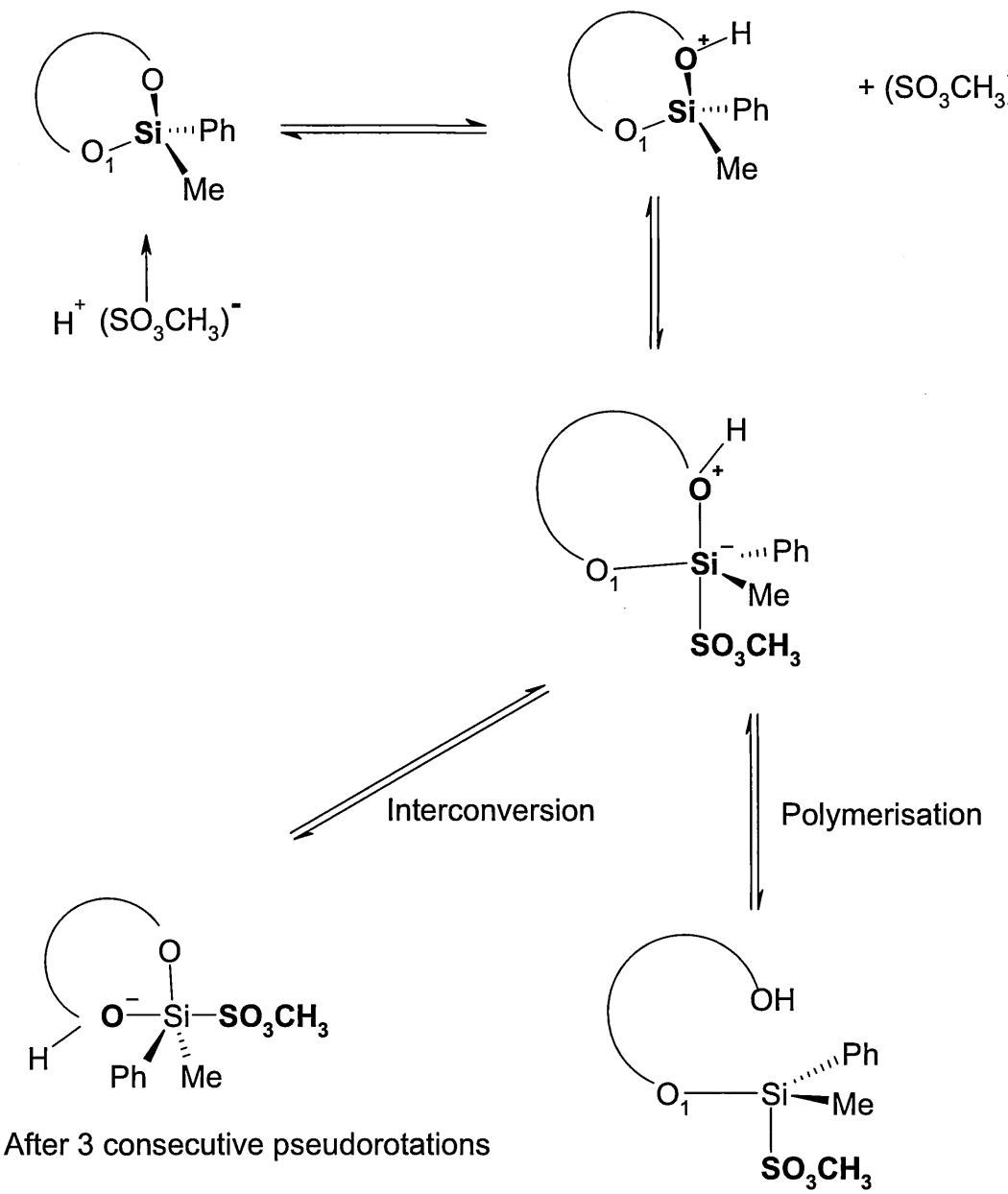


Figure 2.33 Proposed initial steps of interconversion and polymerisation for 2,6-*cis* in a polar aprotic solvent involving the formation of a pentacoordinate silicon intermediate

The protonated pentacoordinate intermediate proposed in Figure 2.33 may be common for both interconversion and polymerisation. When the pentacoordinate intermediate has a long enough life, interconversion products are observed. This occurs through pseudorotation of the stable pentacoordinate silicon intermediate. Polymerisation products are observed when the silicon-oxygen bond is broken in the pentacoordinate

intermediate. The pentacoordinate intermediate is so short lived with mineral acids, such as H_2SO_4, that interconversion products are not observed. Good nucleophiles, e.g. the conjugate base of H_2SO_4, attack the silicon atom and break the Si-O bond rapidly before the pentacoordinate complex can pseudorotate. Silicon-oxygen bond breaking in the pentacoordinate intermediate is relatively slow with methanesulphonic acid, which allows for pseudorotation and interconversion products. The methane sulphonate nucleophile leads to a pentacoordinate intermediate with a reasonable lifetime. This allows pseudorotation to occur, before the Si-Nucleophile bond breaks, to produce the new isomeric product. Nothing happens with very poor nucleophiles as the extent of pentacoordination is small (large energy barriers to pseudorotate) and so Si-O bond cleavage is unlikely, where the Si-Nucleophile bond breaks to give back the starting materials.

The activation energy for polymerisation can be obtained from an Arrhenius plot of similar concentrations of acid over a range of temperatures. The data points selected and their corresponding acid concentrations for the rate constants of polymerisation are based on the sum of 2,6-*cis* + 2,6-*trans* (Table 2.12).

	$[CH_3SO_3H]$ (M) (corrected)	*k (cis+trans)* (1/sec)	ln $[CH_3SO_3H]$ (corrected)	$k/[CH_3SO_3H]^2$ (corrected)	ln $(k/[CH_3SO_3H]^2)$
40°C					
13-1	2.10E-02	3.97E-07	-3.86	9.02E-04	-7.01
13-2	2.05E-02	3.21E-07	-3.89	7.67E-04	-7.17
13-3	1.87E-02	2.80E-07	-3.98	8.01E-04	-7.13
14-1	1.64E-02	1.99E-07	-4.11	7.42E-04	-7.21
14-2	2.33E-02	9.47E-07	-3.76	1.74E-03	-6.35
Ave.				*9.91E-04*	*-6.92*
Std. Dev.					*3.56E-01*
50°C					
11-1	2.07E-02	5.67E-07	-3.88	1.32E-03	-6.63
11-2	1.86E-02	4.61E-07	-3.99	1.33E-03	-6.62
11-3	2.10E-02	4.83E-07	-3.86	1.10E-03	-6.81
12-1	2.35E-02	8.09E-07	-3.75	1.47E-03	-6.53
12-2	1.64E-02	4.93E-07	-4.11	1.84E-03	-6.30
12-3	1.32E-02	3.42E-07	-4.32	1.95E-03	-6.24
Ave.				*1.50E-03*	*-6.50*
Std. Dev.					*2.18E-01*
60°C					
8-1	2.10E-02	7.73E-07	-3.86	1.76E-03	-6.34
8-2	1.64E-02	5.91E-07	-4.11	2.19E-03	-6.12
8-3	2.58E-02	1.44E-06	-3.66	2.17E-03	-6.13
9-1	1.89E-02	7.91E-07	-3.97	2.22E-03	-6.11
9-2	1.40E-02	5.15E-07	-4.27	2.63E-03	-5.94
9-3	1.16E-02	2.65E-07	-4.46	1.96E-03	-6.23
9-4	9.30E-03	1.68E-07	-4.68	1.94E-03	-6.25
10-1	2.32E-02	1.15E-06	-3.76	2.14E-03	-6.14
Ave.				*2.13E-03*	*-6.15*
Std. Dev.					*1.10E-01*
70°C					
5-1	3.28E-02	2.98E-06	-3.42	2.77E-03	-5.89
5-2	2.12E-02	1.67E-06	-3.85	3.73E-03	-5.59
5-3	9.44E-03	4.64E-07	-4.66	5.21E-03	-5.26
6-1	1.64E-02	1.02E-06	-4.11	3.78E-03	-5.58
6-2	1.42E-02	9.07E-07	-4.26	4.53E-03	-5.40
6-3	1.19E-02	7.63E-07	-4.43	5.35E-03	-5.23
7-1	1.88E-02	1.34E-06	-3.98	3.80E-03	-5.57
7-2	2.36E-02	1.98E-06	-3.75	3.55E-03	-5.64
7-3	2.57E-02	4.10E-06	4.10E-06	6.21E-03	-5.08
Ave.				*4.33E-03*	*-5.44*
Std. Dev.					*2.22E-01*

Table 2.12 Polymerisation data for 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of methanesulphonic acid in nitromethane at 40 to 70°C

The data from Table 2.12 were used in the Arrhenius plot (Figure 2.34) to calculate the activation energy as well as the Arrhenius constant for polymerisation.

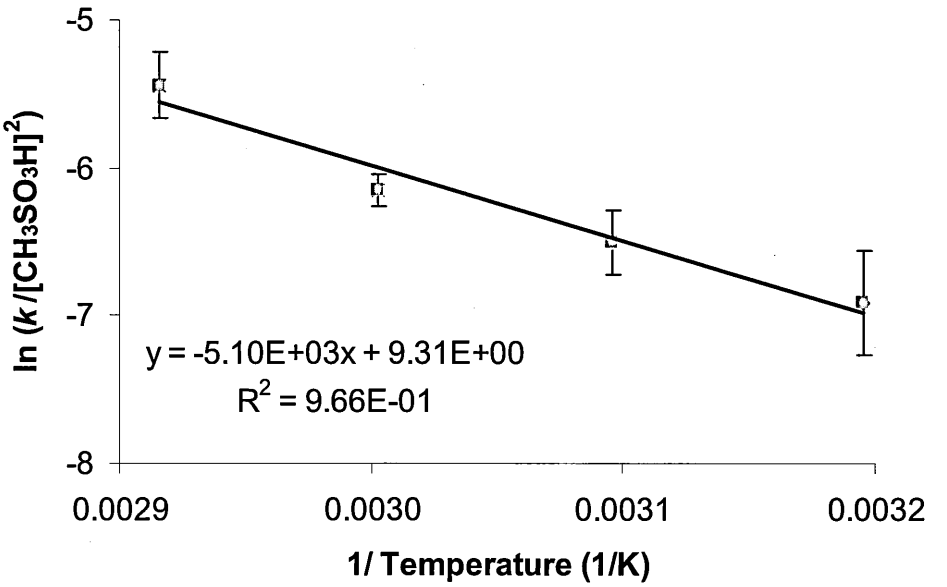


Figure 2.34 Polymerisation of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 23.5 mM methanesulphonic acid in nitromethane at 40 to 70°C

The activation energy for polymerisation based on 2,6-*cis* + 2,6-*trans* is (slope x 8.314 J/mol K) = 42.4 kJ/mol ± 14.2 % catalysed by methanesulphonic acid. This is more than twice the activation energy obtained for interconversion (16.0 kJ/mol) catalysed by methanesulphonic acid. This is consistent with the observation that polymerisation is slower than interconversion. The Arrhenius constant A for polymerisation using 2,6-*cis* + 2,6-*trans* is ($e^{9.31}$) = 11000 ± 14.2 %, where the Arrhenius constant A for methanesulphonic acid catalysed interconversion was several orders of magnitude less (42.9).

A plot of ln (k/T) is a linear function of $1/T$ with the slope of this line = $\Delta H^{\ddagger}/R$, thus $\Delta H^{\ddagger}$ = –slope x R (Figure 2.35). The intercept equals ln(k_B/h) + $\Delta S^{\ddagger}/R$. Thus, $\Delta S^{\ddagger}/R$ = intercept–ln (k_B/h) [note: ln (k_B/h) = 23.76], rearranging to $\Delta S^{\ddagger}_{polym}$ = 8.314 J/ mol K (intercept–23.76).

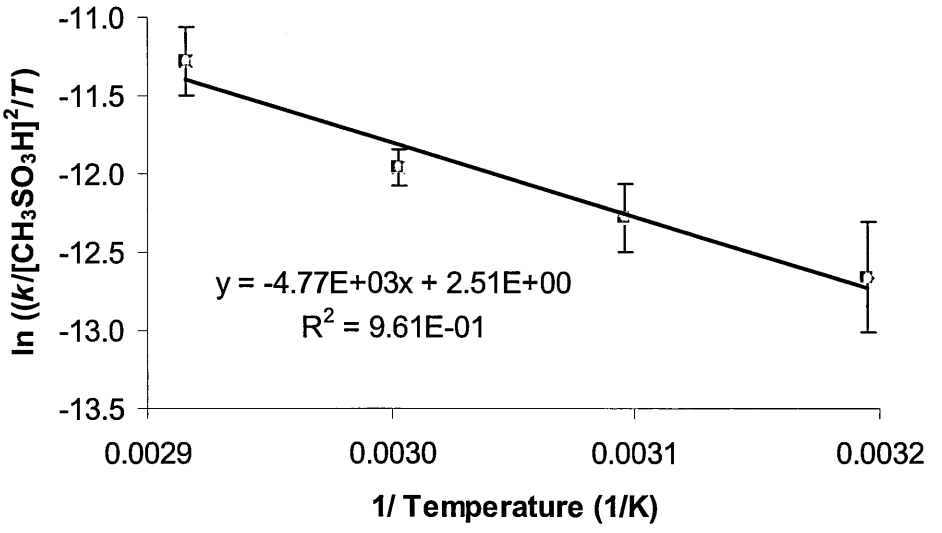


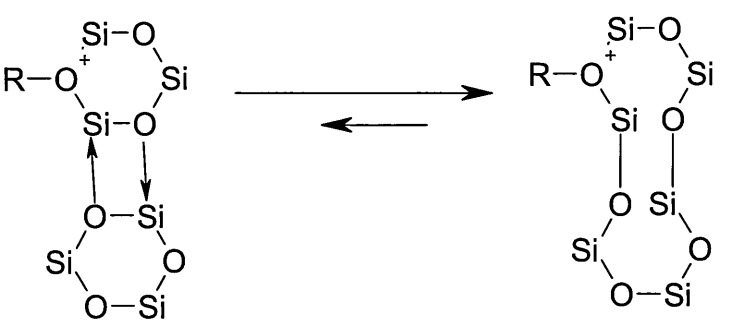
Figure 2.35 Polymerisation of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM (12 mM corrected) methanesulphonic acid in nitromethane at 40 to 70°C

Thus, from Figure 2.35, the entropy of activation for polymerisation $\Delta S^{\ddagger}_{polym}$ = –177 J/mol K ± 14.1 %. The enthalpy of activation for polymerisation $\Delta H^{\ddagger}_{polym}$ = 39.6 kJ/mol ± 14.2 %. The $\Delta S^{\ddagger}_{polym}$ is similar to the entropy of activation calculated for the interconversion reaction catalysed by methanesulphonic acid suggesting a common intermediate. However, the $\Delta H^{\ddagger}_{polym}$ is three times the enthalpy of activation calculated for the interconversion reaction catalysed by methanesulphonic acid.

The kinetics and mechanism of cationic polymerisation of cyclosiloxanes has been studied in more detail over the past 30 years by two groups in particular: one in Poland (Chojnowski et al.) and the other in France (Sigwalt et al.). These studies focused on polymerisation catalysed by triflic acid and trifluoroacetic acid, which is of particular interest as a comparison to the triflic acid catalysed interconversion research in our study.

Some exclusive properties of D_3 polymerisation were uncovered. Chojnowski et al. showed that the polymerisation of D_3 uniquely produces enhancement of cyclics in the D_{3x} pattern.[120, 121] The resulting linear polymers also contain the D_{3x} pattern enhancement.

This systematic pattern is typically not found with D_4 or D_5 triflic acid catalysed polymerisation; no D_{4x} or D_{5x} enhancement is observed. Chojnowski et al. explain this phenomenon by examining the competition between intra- and intermolecular reactions based on the reactivity of the terminal groups. New chain ends form cyclics initially (intramolecular reactions), but as the polymerisation progresses, the chain ends are too far from their origin for ring closure to occur, and intermolecular polymerisation ensues.[60] Sigwalt disagrees with this explanation, mostly due to the lack of formation of systematic products from D_4 polymerisation like those observed in D_3 polymerisation, and that Chojnowski's explanation must include initiation during the entire reaction. Sigwalt instead offers a ring-expansion mechanism which occurs on the oxonium sites of the D_3^+ species to form D_6^+.[66]



The D_6^+ exchanges with the more basic D_3 to re-form the D_3^+ oxonium ion and form D_6. A back-biting mechanistic explanation is dismissed because back-biting is a random process that produces a mixture of cyclosiloxanes. Also, back-biting of a D_3 produced polymer and a D_4 produced polymer results in a similar distribution of products. *Ab initio* calculations performed by Grigoras and Lane on disiloxane and hexamethyldisiloxane showed the electronic charge from the lone pair on oxygen is transferred to the covalent bonding region between silicon and oxygen.[20] This diminishes the lone pair on oxygen. This charge distribution may be more difficult in the strained D_3 Si–O–Si bond angle than in D_4. Therefore, less charge is between Si and O with D_3 and more charge is located on

oxygen, making D_3 more basic than D_4. The D_3 polymerisation products may be explained by the basicity of D_3, where D_3 may preferentially react because it is the most basic species in the system. This may not be the case with D_4 and could help explain the differences observed in the polymerisation between D_3 and D_4 cyclosiloxanes. The results of Chojnowski et al. support this, where they showed that trifluoroacetic acid binds more strongly with the oxygen in D_3 than in D_4 in a dichloromethane solution.[60] These intricacies of D_3 and D_4 polymerisation provide insight into the mechanism of polymerisation, but are not entirely pertinent to our research of cyclosiloxane interconversion. The kinetics and the proposed species (e.g. acid-water, acid-substrate, acid-acid, and other complexes) occurring during the polymerisation reaction are more interesting as insight into the interconversion studied under similar conditions.

Polymerisation occurs through acid catalysed ring-opening, where the detailed mechanism is still not completely understood.[28, 64, 100] The products we observed under these conditions are consistent with the findings other researchers have published regarding the acid catalysed ring-opening polymerisation of cyclosiloxanes. Wilczek and Chojnowski studied the kinetics of trifluoroacetic acid catalysed ring opening of D_3/D_4 in dichloromethane (CH_2Cl_2) and *n*-heptane, and proposed that three processes are involved in the mechanism.[60]

$$HA + SiOSi \rightarrow SiA + HOSi \qquad (1)\ \text{acidolysis}$$

$$SiOH + SiOH \rightarrow SiOSi + H_2O \qquad (2)\ \text{condensation}$$

$$SiA + H_2O \rightarrow SiOH + HA \qquad (3)\ \text{hydrolysis}$$

HA represents the acid, where A = CF_3COO in this case. The siloxane bond is broken by acid in (1) and by water in reverse (2), both referred to as acidolysis. Condensation occurs in (2) and in reverse (1). The authors determined that the addition of water strongly increases ester formation (Si-$OCOCF_3$) by acidolysis (1). The addition of silanol and

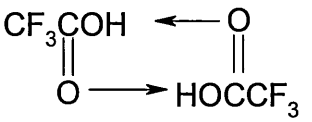
water has the same effect on the rate of polymerisation. This supports acidolysis (1), and that its equilibrium is achieved fast relative to polymerisation.[67] Acidolysis breaks a Si–O bond and results in ring-opening of the cyclosiloxane to form the ester and silanol. Acidolysis is not proposed to occur with interconversion because the resulting linear siloxanes are not observed. If the SiA groups are formed in (1) without water, then these SiA groups (esters when triflic acid is used) require activation to polymerise. Chojnowski et al. showed that in the absence of water, esterification of the silanol from (1) to form water and the silyl ester (reverse (3)) is faster than acidolysis (1).[60] Both ends of the opened cyclic will undergo esterification in the absence of water. This could be used to explain second order in acid. Sigwalt suggests that triflic acid may be involved in the propagation step as well, in order to account for the higher orders in acid.

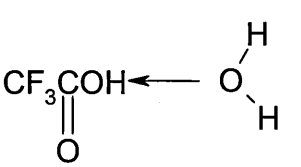
The order in either triflic or trifluoroacetic acid during polymerisation has been determined to be in the range of 2 to 3. Hydrogen bonded acid complexes are proposed as catalysts in cyclosiloxane polymerisation. These species are responsible for proton transfer to the oxygen of the siloxane in acid catalysed cyclosiloxane polymerisation.

HA + Base ←→AH•••Base

Where Base= H_2O, SiOH, HA, SiA

Wilczek and Chojnowski suggest that hydrogen bonded trimers act as the proton donors in polymerisation of cyclosiloxanes. Wilczek and Chojnowski used IR spectroscopy to show that the acid is predominately in the form of a dihydrogen-bonded complex, but only as a single hydrogen-bonded complex with water.





These complexes and larger hydrogen-bonded acid aggregates may be responsible for the

multiple orders in catalyst that were observed with polymerisation. Hydrogen-bonded complexes (specifically acid-siloxane, and acid-water were shown) are weaker in dichloromethane than in the heptane solvent (competitive interaction of acid with the more polar dichloromethane). Addition of water increases the concentration of free acid (3), producing more active centres in (1). This may explain the increase in the rate of polymerisation upon addition of water, which is discussed further in Chapter 3.

Wilczek and Chojnowski suggest that the triflate ion favours onium ion active centre formation. Weaker acids (for example, CF_3COOH) have acid-acid interactions and other H-bonded species (acid-substrate). The strong triflate-substrate interactions diminish the acid-acid interactions with a higher tendency to form silyl esters (1).[65] In our interconversion reactions, the triflate-substrate interaction may occur to form a pentacoordinate transition state, but probably not form the silyl esters as polymerisation products would be expected from this ring-opened product.

The negative entropy ($-\Delta S^{\ddagger}$ for all reactions) we have observed is consistent with a loss of degrees of freedom in the rate limiting step of the reaction. A pentacoordinate silicon species would be consistent with this increased order. Overall, the Arrhenius constant is small and suggests a highly oriented reaction. These results, including the activation energy, are similar to the triflic acid results and typical ring-opening polymerisation of cyclosiloxanes.

The shape of the kinetic curves for cyclosiloxane polymerisation is complex and Chojnowski suggests the reaction proceeds according to a complex kinetic law that cannot be analysed according to simple order of chemical reactions. Chojnowski uses initial rate analysis to avoid some of these complications and those from the reverse processes (back-biting). Chojnowski et al. measured the initial rate of polymerisation of D_4 catalysed by triflic acid as: [64]

$$k_p = [CF_3SO_3H]^{2.2} [D_4]^{0.7}$$

Higher conversions show first-order dependence on D_4, and an order in catalyst of 2.7 with both D_4 and D_6 starting material, as shown by Sigwalt, et al.[62] We will show $k_{interconversion} = [CF_3SO_3H]^1 [D_4]^1$ in the next section (Section 2.3.2). Sigwalt obtained $[TfOH]^{2.7}$ from polymerisation of 0.27 - 2.8 M $[D_4]$ $1.5x10^{-3}$ - $1.2x10^{-2}$ M [TfOH] using gas-liquid chromatography (GLC).[66] Both Sigwalt and Chojnowski propose hydrogen bonded complexes to account for the multiple order in acid as well as the rate increases observed with the addition of water. These hydrogen-bonded species can quickly disperse charge, formed as a result of proton transfer, through hydrogen-bond migration.

An induction period for polymerisation has been observed at low catalyst concentrations. Sigwalt et al. observed an induction period lasting several hours at low concentrations of triflic acid and several minutes for 0.966 M D_4 catalysed by 5.85 mM triflic acid in CH_2Cl_2.[122] Chojnowski et al. reported a 27 kJ mol^{-1} activation energy for the polymerisation of 1.5 M D_4 in CH_2Cl_2 catalysed with 0.3 mM triflic acid at 30°C. [64] The activation energy increased to 67 kJ mol^{-1} with the addition of 70 mM water. They determined that the polymerisation was first-order in D_4 and second-order in acid. The order in acid decreased to 1.3 as water was added. The mechanism is hypothesised to change with the addition of water as the water frees the acid from the D_4, which is the SiA ester complex.

The authors suggest that the formation of H-bonded complexes, such as acid-acid and the competition between H-bonded complexes and acid-monomer complexes are the reasons for some of the kinetic results, i.e. multiple and partial orders. Wilczek and Chojnowski showed that stronger acids exhibit a higher tendency to form the silyl esters.[65] The ring-opened silyl esters were not observed in the interconversion reaction, as typical ring-opened products were not produced.

Our results support a common pentacoordinate silicon compound for both interconversion and polymerisation. Pseudorotation of the pentacoordinate silicon compound is proposed as the mechanistic pathway for the interconversion reaction. Silicon-oxygen bond breaking results in polymerisation. The stability, and possibly lifetime, of the pentacoordinate intermediate controls the balance between polymerisation and interconversion. The study of interconversion catalysed by a stronger acid, triflic acid, is discussed next in order to further analyse this hypothesis and directly probe the impact of the nucleophile on the proposed pentacoordinate species and the balance between interconversion and polymerisation.

2.3.2 Evaluation of Trifluoromethanesulphonic Acid Catalysed Interconversion

The interconversion reaction was attempted with triflic acid over a range of catalyst concentrations. The conversion from 2,6-*cis* in nitromethane to an approximately equimolar mixture of the 2,6-*cis* and 2,6-*trans* cyclosiloxanes was followed by the GC method discussed previously.

2.3.2.1 Variable Temperature Study with Trifluoromethanesulphonic Acid

Interconversion catalysed by triflic acid in treated GC vials was studied as a function of temperature. A reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane (20 mM) in nitromethane solvent was catalysed by a range of triflic acid concentrations (0.6 to 1.4 mM) over a 40 to 70°C temperature range. The reactions consistently proceeded to the 49.8%:50.2% 2,6-*cis*:2,6-*trans* equilibrium. The GC data and corresponding isomer concentrations are contained in Appendix A. A plot for each reaction of ln [2,6-*cis*] versus time as a representation of 80% reaction completion produces a straight line, where the slope represents the rate constant, k (e.g. Figure 2.6, Figure 2.7). Good linearity of these

plots confirmed that the reaction is first-order with respect to the cyclosiloxane starting material, 2,6-*cis*. Thus, $x = 1$ for the order in 2,6-*cis* starting material according to $J = k$ [2,6-*cis*]^x [catalyst]^y. The order with respect to 2,6-*cis* starting material is the same as was found for the interconversion reaction catalysed by methanesulphonic acid.

The rate constants (s^{-1}) for each reaction, using the various catalyst concentrations and temperatures, were calculated using the same method according to the GC data found in Appendix A, and the results are listed in Table 2.13.

Sample #	[Triflic Acid] (mol/L)	[Triflic Acid] (mol/L) (corrected)	*k* (1/sec) (production of *trans*)	*k* (1/sec) (-loss of *cis*)
40°C				
148-3	8.03E-04	5.30E-05	2.72E-05	2.64E-05
149-1	9.90E-04	2.40E-04	7.48E-05	7.58E-05
149-2	9.08E-04	1.58E-04	3.96E-05	3.99E-05
149-3	1.32E-03	5.72E-04	1.94E-04	1.93E-04
150-1	1.12E-03	3.71E-04	1.00E-04	9.94E-05
150-2	1.32E-03	5.66E-04	1.77E-04	1.72E-04
150-3	1.41E-03	6.63E-04	2.06E-04	2.03E-04
50°C				
151-3	1.02E-03	1.92E-04	9.02E-05	9.00E-05
152-3	1.12E-03	2.88E-04	9.00E-05	9.08E-05
153-1	1.20E-03	3.74E-04	1.21E-04	1.24E-04
153-2	1.31E-03	4.81E-04	1.94E-04	1.92E-04
60°C				
155-3	7.99E-04	2.69E-04	1.16E-03	1.17E-03
155-4	6.33E-04	1.03E-04	5.20E-04	5.22E-04
160-4	9.31E-04	4.01E-04	2.82E-04	2.81E-04
2-1	8.68E-04	3.38E-04	1.15E-04	1.15E-04
70°C				
157-3	6.30E-04	2.60E-04	1.60E-04	1.61E-04
158-1	7.77E-04	4.07E-04	3.43E-04	3.42E-04
3-1	8.20E-04	4.50E-04	3.39E-04	3.40E-04
3-2	6.98E-04	3.28E-04	3.84E-05	4.98E-05
3-3	7.39E-04	3.69E-04	6.02E-05	6.02E-05
3-4	8.93E-04	5.23E-04	1.14E-04	1.15E-04

Table 2.13 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of triflic acid in nitromethane at 40 to 70°C

The minimum concentration of catalyst required before product was observed was obtained from a linear fit of a plot of the acid concentration versus the rate constant

(Figure 2.36) for the 40°C interconversion using the loss of 2,6-*cis* isomer data.

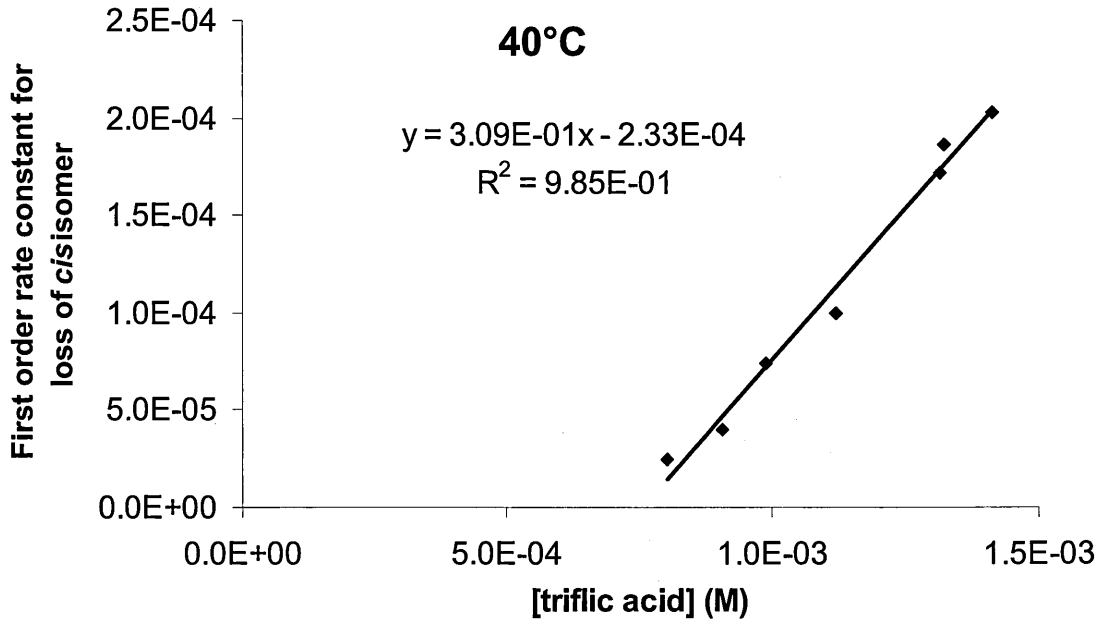


Figure 2.36 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of triflic acid in nitromethane at 40°C

A linear relationship of catalyst concentration and the rate constant of interconversion were observed. The x-axis intercept is an extrapolation of the concentration of catalyst that is "inactive" toward interconversion, determined to be 0.75 mM for the reaction based on the loss of the 2,6-*cis* isomer. This correction accounts for nearly half of the catalyst added. A much smaller correction was necessary with the methanesulphonic acid data, as twenty times more catalyst was used and the "inactive" catalyst was only a small percentage of the total catalyst. An "inactive" catalyst concentration was still observed using the treated GC reaction vessels, when catalysed by triflic acid. Similar calculations were performed using the rate constant data at the other temperatures and the results are contained in Table 2.14. This amount of inactive catalyst will be subtracted from the initial concentration of catalyst added.

Temperature (°C)	Triflic acid (mM) (loss of 2,6-*cis*)	Triflic acid (mM) (production of 2,6-*trans*)
40	0.75	0.76
50	0.82	0.82
60	0.50	0.50
70	0.36	0.36

Table 2.14 Calculated inactive catalyst from the interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of triflic acid in nitromethane at 40 to 70°C

The concentration of inactive catalyst appears to decrease with increasing temperature according to Table 2.14. This is an unexpected result, as a similar amount of inactive catalyst should be present at each temperature. The amount of data available for the 60 and 70°C interpretation is minimal due to the increased rate of the reaction. Also, the reactions performed at each temperature were prepared with a separate dilution of a new stock catalyst solution; inducing a different, albeit minimal, error at each temperature.

Table 2.15 contains the corrected concentration of catalyst for each corresponding temperature and the rate constant results for the interconversion under the specified conditions. The data that used old stock catalyst solution has been discarded due to changes observed in the triflic acid stock solution. This is presumably due to the high moisture sensitivity of triflic acid.

Sample #	[Triflic Acid] (mol/L)	[Triflic Acid] (mol/L) (corrected)	*k* (1/sec) (production of *trans*)	*k* (1/sec) (-loss of *cis*)	ln corrected [Triflic Acid]	ln *k* (-loss of *cis*)
40°C						
148-3	8.03E-04	5.30E-05	2.72E-05	2.64E-05	-9.84	-10.54
149-1	9.90E-04	2.40E-04	7.48E-05	7.58E-05	-8.33	-9.49
149-2	9.08E-04	1.58E-04	3.96E-05	3.99E-05	-8.75	-10.13
149-3	1.32E-03	5.72E-04	1.94E-04	1.93E-04	-7.47	-8.55
150-1	1.12E-03	3.71E-04	1.00E-04	9.94E-05	-7.90	-9.22
150-2	1.32E-03	5.66E-04	1.77E-04	1.72E-04	-7.48	-8.67
150-3	1.41E-03	6.63E-04	2.06E-04	2.03E-04	-7.32	-8.50
50°C						
151-3	1.02E-03	1.92E-04	9.02E-05	9.00E-05	-8.56	-9.32
152-3	1.12E-03	2.88E-04	9.00E-05	9.08E-05	-8.15	-9.31
153-1	1.20E-03	3.74E-04	1.21E-04	1.24E-04	-7.89	-9.00
153-2	1.31E-03	4.81E-04	1.94E-04	1.92E-04	-7.64	-8.56
60°C						
160-4	9.31E-04	4.01E-04	2.82E-04	2.81E-04	-7.82	-8.18
2-1	8.68E-04	3.38E-04	1.15E-04	1.15E-04	-7.99	-9.07
70°C						
157-3	6.30E-04	2.60E-04	1.60E-04	1.61E-04	-8.25	-8.73
158-1	7.77E-04	4.07E-04	3.43E-04	3.42E-04	-7.81	-7.98
3-1	8.20E-04	4.50E-04	3.39E-04	3.40E-04	-7.71	-7.99

Table 2.15 Rate constants from the interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by similar concentrations of triflic acid in nitromethane at 40 to 70°C

The order with respect to catalyst was determined from a logarithm of the rate constant versus a logarithm of "corrected" catalyst concentration plot. The catalyst concentration was corrected by subtraction of the inactive concentration at each temperature, e.g. 0.75 mM triflic acid for the 40°C interconversion. First-order kinetics best describes the reaction under these conditions, where 0.86 (Figure 2.37) order with respect to triflic acid is obtained for the 40°C interconversion.

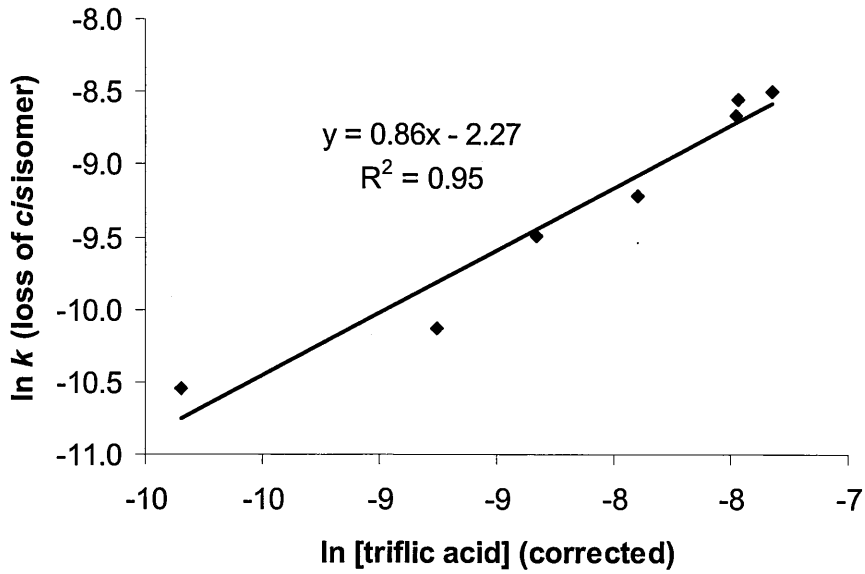


Figure 2.37 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of triflic acid (corrected) in nitromethane at 40°C

A similar plot to that in Figure 2.37 with the 50°C interconversion data results in a 0.84 order with respect to triflic acid after subtraction of the inactive 0.83 mM catalyst. The 60 and 70°C logarithm of the rate constant versus a logarithm of catalyst concentration plots both result in a 1.02 slope after the appropriate inactive catalyst concentrations are subtracted, which also indicates these reactions are approximately first-order. Thus, the orders with respect to starting material and catalyst are both first-order for "corrected' triflic acid catalysed interconversion of 2,6-*cis* over the 40 to 70°C temperature range evaluated. Thus, $x = 1$ and $y = 1$ according to $J = k$ [2,6-*cis*]^x [catalyst]^y. These results are specific to the catalyst concentration and solvent conditions shown. The results presented above along with the constant ([2,6-*cis*] + [2,6-*trans*]) data given in Appendix A show interconversion without ring-opened products is occurring with triflic acid. First order in catalyst suggests that only one molecule of catalyst participates in the rate determining step of the reaction. Each triflic acid molecule may provide both a proton

and a triflate nucleophile. Only the proton appears to be involved in the mechanism of interconversion, as will be shown by the proton sponge results discussed in Section 2.3.2.2.

From Table 2.13 the data where the concentrations of acid was selected from each temperature, Samples 150-2, 153-2, 160-4, and 158-1. The data are retabulated (Table 2.16) for the interconversion of 2,6-*cis* based on the loss of 2,6-*cis*.

Sample #	[Triflic Acid] (mol/L)	[Triflic Acid] (mol/L) (corrected)	*k* (1/sec) (production of *trans*)	*k* (1/sec) (-loss of *cis*)	ln corrected [Triflic Acid]	ln *k* (-loss of *cis*)	ln (*k*/ [Triflic Acid]) (-loss of *cis*)	ln ((*k*/ [Triflic Acid])/*T*)
40°C								
148-3	8.03E-04	5.30E-05	2.72E-05	2.64E-05	-9.84	-10.54	-0.70	-6.44
149-1	9.90E-04	2.40E-04	7.48E-05	7.58E-05	-8.33	-9.49	-1.15	-6.90
149-2	9.08E-04	1.58E-04	3.96E-05	3.99E-05	-8.75	-10.13	-1.37	-7.12
149-3	1.32E-03	5.72E-04	1.94E-04	1.93E-04	-7.47	-8.55	-1.09	-6.83
150-1	1.12E-03	3.71E-04	1.00E-04	9.94E-05	-7.90	-9.22	-1.32	-7.06
150-2	1.32E-03	5.66E-04	1.77E-04	1.72E-04	-7.48	-8.67	-1.19	-6.94
150-3	1.41E-03	6.63E-04	2.06E-04	2.03E-04	-7.32	-8.50	-1.18	-6.93
Ave.							*-1.14*	*-6.89*
Std. Dev.							*0.22*	*0.22*
50°C								
151-3	1.02E-03	1.92E-04	9.02E-05	9.00E-05	-8.56	-9.32	-0.76	-6.54
152-3	1.12E-03	2.88E-04	9.00E-05	9.08E-05	-8.15	-9.31	-1.15	-6.93
153-1	1.20E-03	3.74E-04	1.21E-04	1.24E-04	-7.89	-9.00	-1.10	-6.88
153-2	1.31E-03	4.81E-04	1.94E-04	1.92E-04	-7.64	-8.56	-0.92	-6.70
Ave.							*-0.98*	*-6.76*
Std. Dev.							*0.18*	*0.18*
60°C								
155-3	7.99E-04	2.69E-04	1.16E-03	1.17E-03	-8.22	-6.75	1.47	-4.34
155-4	6.33E-04	1.03E-04	5.20E-04	5.22E-04	-9.18	-7.56	1.62	-4.19
160-4	9.31E-04	4.01E-04	2.82E-04	2.81E-04	-7.82	-8.18	-0.36	-6.16
2-1	8.68E-04	3.38E-04	1.15E-04	1.15E-04	-7.99	-9.07	-1.08	-6.89
Ave.							*-0.72*	*-6.53*
Std. Dev.							*0.26*	*0.26*
70°C								
157-3	6.30E-04	2.60E-04	1.60E-04	1.61E-04	-8.25	-8.73	-0.48	-6.32
158-1	7.77E-04	4.07E-04	3.43E-04	3.42E-04	-7.81	-7.98	-0.17	-6.01
3-1	8.20E-04	4.50E-04	3.39E-04	3.40E-04	-7.71	-7.99	-0.28	-6.12
3-2	6.98E-04	3.28E-04	3.84E-05	4.98E-05	-8.02	-9.91	-1.88	-7.72
3-3	7.39E-04	3.69E-04	6.02E-05	6.02E-05	-7.90	-9.72	-1.81	-7.65
3-4	8.93E-04	5.23E-04	1.14E-04	1.15E-04	-7.56	-9.07	-1.51	-7.35
Ave.							*-0.31*	*-6.15*
Std. Dev.							*0.16*	*0.16*

Table 2.16 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by similar concentrations of triflic acid at various temperatures in nitromethane

The Arrhenius plot of these data (Figure 2.38) was used to obtain the activation energy and Arrhenius constant from the equation of the linear fit, as discussed above for the interconversion based on the loss of the 2,6-*cis* isomer.

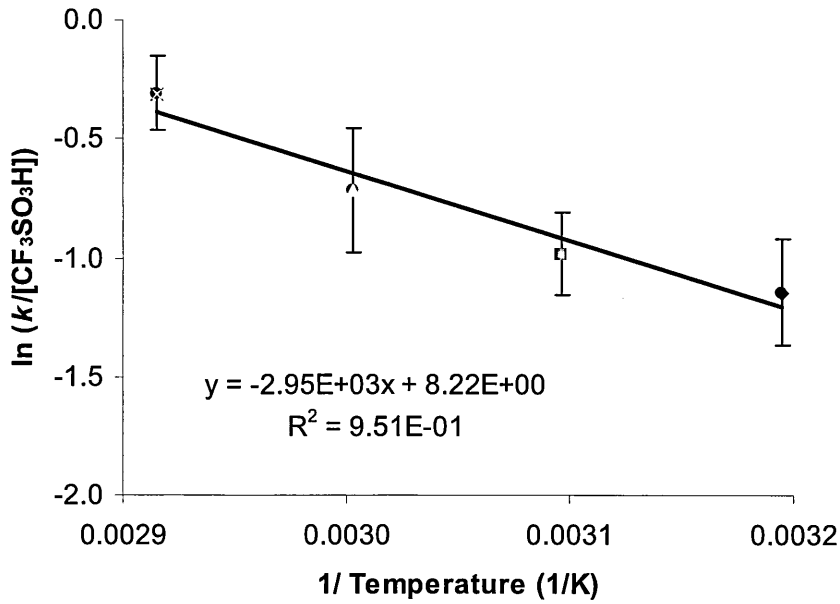


Figure 2.38 Arrhenius plot for the interconversion reaction of 20 mM 2,6-*cis*-diphenyl-hexamethylcyclotetrasiloxane based on the loss of the 2,6-*cis* isomer when catalysed by similar concentrations of triflic acid in nitromethane at various temperatures

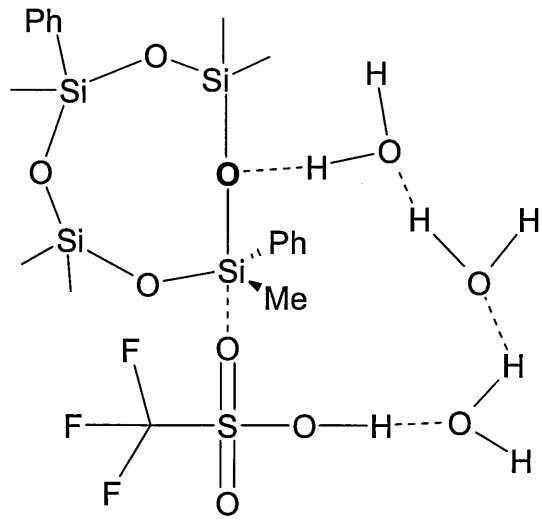
The activation energy for the interconversion based on the loss of 2,6-*cis* isomer is (slope x 8.314 J/mol K) = 24.5 kJ mol^{-1} ± 9.9 % from Figure 2.38. A similar activation energy (16.0 kJ/mol) was observed for the interconversion reaction catalysed by methanesulphonic acid. The Arrhenius constant *A* for the loss of 2,6-*cis* isomer is ($e^{8.22}$) = 3710 ± 9.9 %. The extrapolation method used for the Arrhenius constant imparts a large error similar to that of the methanesulphonic acid results. Overall, the Arrhenius constant is small and suggests a highly oriented reaction. These results, including the activation energy, are similar to the methanesulphonic acid results and typical for ring-opening polymerisation of cyclosiloxanes even though the catalyst concentrations are so different.

The activation energy calculated above for the interconversion reaction catalysed by triflic acid is lower than what has been commonly reported for the polymerisation of cyclosiloxanes. Fang et al. studied the 1.99% cationic polymerisation of 96.7% D_4 capped with 3.3% MM (hexamethyldisiloxane) over a 40C to 70°C temperature range.[123] They

were specifically analysing the formation of rings, and they separated D_4 from the formation of all other rings, D_x. Fang et al. assumed that rings are mainly produced by back-biting and that different size rings are formed at similar rates for the kinetic analysis of this neat polymerisation. Their analysis resulted in an activation energy for D_4 production of 37.8 kJ mol^{-1} and E_a for all other D_x units was determined to be 39.2 kJ mol^{-1}. Chojnowski and Wilczek studied the polymerisation of 2.0 M D_3 in dichloromethane with 5.0 x 10^{-4} M triflic acid catalyst.[67] In the absence of water a negative activation energy (–25 kJ/mol), a negative order (–0.7) with respect to cyclosiloxane, and an unusually low Arrhenius factor ($10^{-8}s^{-1}$) was observed. When water (3.1 x 10^{-2} M) was added, the activation energy was 50 kJ/mol and first order in cyclosiloxane, and an increase in the rate of polymerisation was observed. Wilczek et al. later showed a threefold increase in the rate of the 7.0 x 10^{-4} M triflic acid catalysed polymerisation of 1.5 M D_4 with the addition of 5.0 x 10^{-3} M water at 30°C.[64] An activation energy of 27 kJ/mol was measured without water, increasing to 67 kJ/mol with the addition of 7.0 x 10^{-3} M water. The data from Wilczek and Chojnowski show that water in small amounts increases the polymerisation rate of cyclosiloxanes. Kendrick observed no catalysis of polymerisation by either anhydrous HCl or iron chloride without water. Ab initio calculations yield results in accordance with the findings of Wilczek and Chojnowski, showing that the activation barrier as a function of water concentration is the lowest with four molecules of water in the protonated species.

Some of the learnings from polymerisation may be applied to the interconversion reaction. The acidolysis step (1) is not applicable to form the silyl ester and silanol, as the ring would be broken and polymerisation would ensue. The interconversion of 2,6-*cis* was determined to be first order in triflic acid and when more than four moles of water per mole of acid were used, a reduction in the rate constant was observed. The hydrogen

bonded complex of triflic acid with 2,6-diphenylhexamethylcyclotetrasiloxane may look like:



This complex facilitates the protonation of the siloxane oxygen. Depending on the choice of solvent, a solvent molecule may be able to participate as a hydrogen-bonded species possibly replacing a water molecule in the above structure.

The nucleophile attacks the silicon to form a pentacoordinate intermediate. A backside attack would cause inversion of configuration about the silicon atom if there were a good leaving group in the opposite axial position to the nucleophile in the last molecule of Figure 2.33. At this point, the breaking of the silicon to protonated oxygen bond would provide a mechanistic pathway for the ring-opening polymerisation that is observed with the stronger nucleophiles. The silanol polymerises through condensation, which is enhanced by solvation of a polar solvent. This bond breaking leads to polymerisation and does not support a ring-opening interconversion mechanism, unless intramolecular ring closure is faster than polymerisation.

If the nucleophile and the leaving group on silicon were the same (e.g. methoxy) this would provide a path for the racemisation Sommer observed in methanol.[112] Under conditions of only interconversion of 2,6-*cis* this siloxane bond is not broken, otherwise polymerisation would ensue. Pseudorotation is suggested to account for interconversion

without siloxane bond breaking. The activation energy for polymerisation without water (27 kJ/mol) is similar to that obtained from the interconversion of 2,6-*cis* catalysed by triflic acid in our study, which may support a common intermediate. The above discussion shows that the presence of small amounts of water can dramatically impact the rate of polymerisation, and actually the amount of water can cause a different effect. There are also differences between D_3 and D_4 polymerisation that must be considered and it may not be appropriate to compare them as equals. The role of water will be discussed in more detail in Chapter 3.

The Eyring plot for the interconversion reaction of 2,6-*cis* is shown in Figure 2.39.

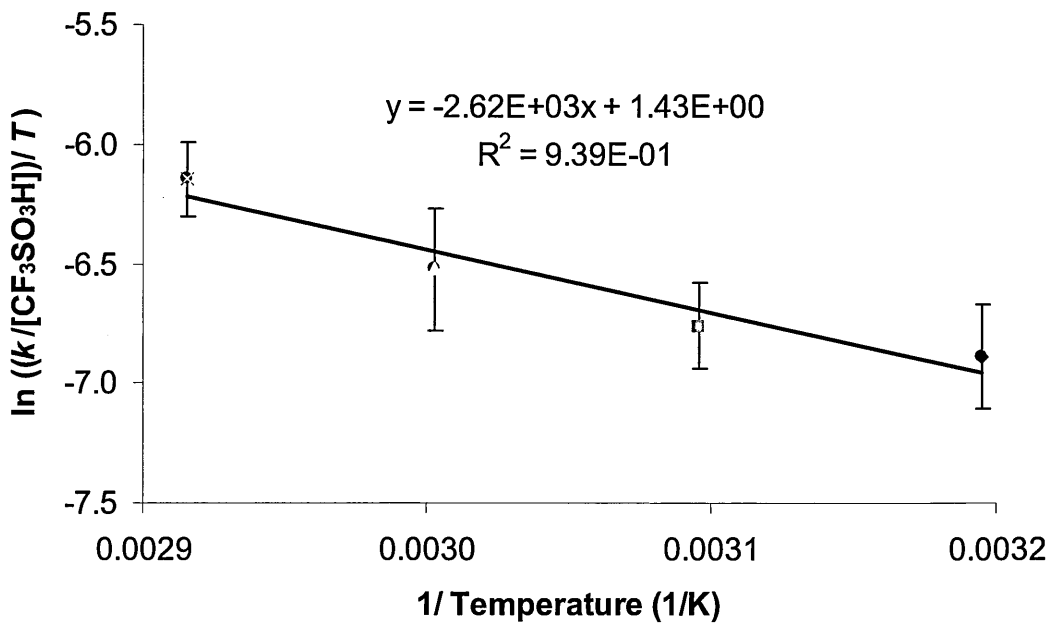


Figure 2.39 Eyring plot for the interconversion reaction of 20 mM 2,6-*cis*-diphenyl-hexamethylcyclotetrasiloxane based on the loss of the 2,6-*cis* isomer when catalysed by similar concentrations of triflic acid in nitromethane at various temperatures

From Figure 2.39, the entropy of activation $\Delta S^{\ddagger}$ is –186 J/mol K ± 9.8 % and the enthalpy of activation $\Delta H^{\ddagger}$ is 21.8 kJ/mol ± 9.8 %. Such a large and negative entropy suggests that the reaction proceeds through a highly ordered transition state. A pentacoordinated silicon

species would be a more ordered complex, and the entropy of reaction would thus decrease in accordance with the results. These results are very similar to the methanesulphonic acid catalysed interconversion reactions, where the entropy of activation $\Delta S^{\ddagger}$ is –222 J/mol K and the enthalpy of activation $\Delta H^{\ddagger}$ is 13.2 kJ/mol.

The interconversion of 2,6-*cis* catalysed by triflic acid in nitromethane was shown in our study to obey first-order kinetics with respect to the starting material in the nitromethane system. The catalyst concentration study was limited by the earlier observance of polymerisation products at higher acid concentrations, limiting the collection of data on interconversion. At higher catalyst concentrations polymerisation products were observed, and the range available for observation of the interconversion reduced because the rates of both reactions were increased. Triflic acid catalysed interconversion occurs with much lower concentrations of catalyst than methanesulphonic acid and the range studied shows less interference of polymerisation.

2.3.2.2 Proton Sponge

The data from above show that the interconversion reaction is catalysed by triflic acid. Frye and Spielvogel were unsuccessful in their attempts at interconversion with protic acids. Triflic acid is known to induce the polymerisation of cyclosiloxanes.[59] Protonation of the siloxane oxygen is the generally agreed first step of the mechanism for the polymerisation of cyclosiloxanes with Brönsted acids.[49] The first step cannot occur if the proton is captured or removed. Brown and Kanner first reported the use of hindered pyridines to differentiate between protic and Lewis acids.[71] "Proton sponges" of the hindered amine and pyridine type display an unusual basicity but poor nucleophilicity due to the steric hindrance around the amino groups.[72] Hindered pyridines or diamines are non-nucleophilic bases capable of stopping the reactions initiated by protonation by

trapping the protons.[73] The use of proton sponges can thus provide some insight (i.e. the necessity of protons) into this interconversion mechanism.

The proton sponge 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) was used in an interconversion reaction catalysed by triflic acid. The proton sponge was added to a triflic acid catalysed interconversion reaction of 20 mM 2,6-*cis*. When the protons are bound by the proton sponge no reaction should occur if any step of the mechanism of interconversion is protonation of the siloxane oxygen. This is what was observed when a proton trap was added to the interconversion of 2,6-*cis* catalysed by triflic acid (Figure 2.40).

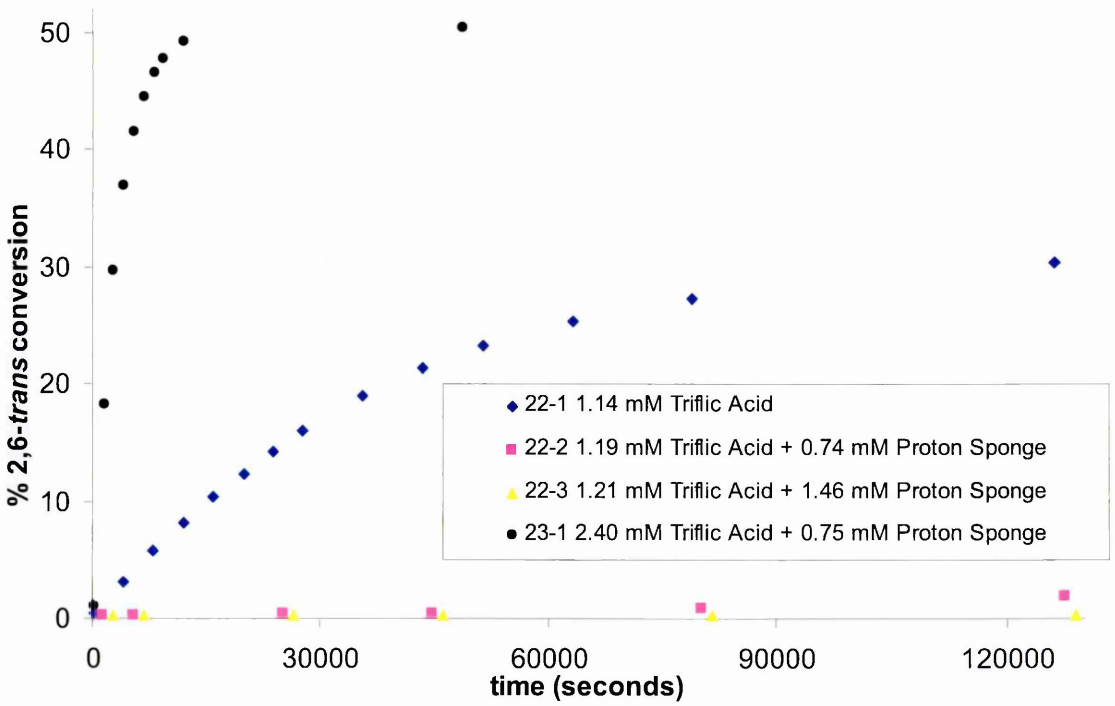


Figure 2.40 Interconversion of 20 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by triflic acid in nitromethane at 40°C with DBMP as a proton sponge

The addition of the proton sponge stopped or reduced the rate of the interconversion reaction catalysed by triflic acid. No interconversion or polymerisation

was observed during the time scale studied when two moles or more of proton sponge was added to three moles of triflic acid. The proton sponge captured the proton from the triflic acid and prevented it from protonating the siloxane oxygen of the 2,6-*cis* molecule. The interconversion was still able to achieve completion when only one mole of proton sponge was added for every three moles of triflic acid (Sample 23-1). The proton sponge greatly reduced the rate (prevented interconversion over the time scale studied) of the reaction when two moles of proton sponge was added for every three moles of triflic acid (Sample 22-2) or more (1:1 in 22-3). The rate of interconversion was reduced when lower molar concentrations of proton sponge to triflic acid were added (1:3 in Sample 23-1).

A proton is necessary for the interconversion reaction catalysed by triflic acid. The control interconversion reaction (Sample 22-1) without proton sponge does not achieve equilibrium under the time scale studied. A portion of the catalyst does not appear to be active toward interconversion, as is consistent with the previously determined concentration of "inactive" catalyst. This may explain why a lower molar amount of proton sponge to catalyst prevents the interconversion reaction.

The result that the proton sponge prevents the interconversion reaction catalysed by triflic acid shows that the proton is necessary. First order in triflic acid was determined earlier and the proton sponge results suggest that the proton is involved in the transition state of the mechanism. Second order in methanesulphonic acid was observed, resulting in both the proton and the methanesulphonate ions being involved in the transition state of the mechanism. The change to first order in catalyst with triflic acid shows that the weaker triflate ion is not involved in the mechanism. The nucleophile for triflic acid catalysed interconversion may be the solvent, since it is in excess and not in the observed rate equation. A pentacoordinate intermediate is proposed in Figure 2.41, which accounts for the rate equation: $J = k\,[2,6\text{-}cis]^1\,[\text{triflic acid}]^1$, or more precisely,

$J = k\,[2,6\text{-}cis]^1\,[H^+]^1$, where possibly $k = k'\,[CH_3NO_2]^n$.

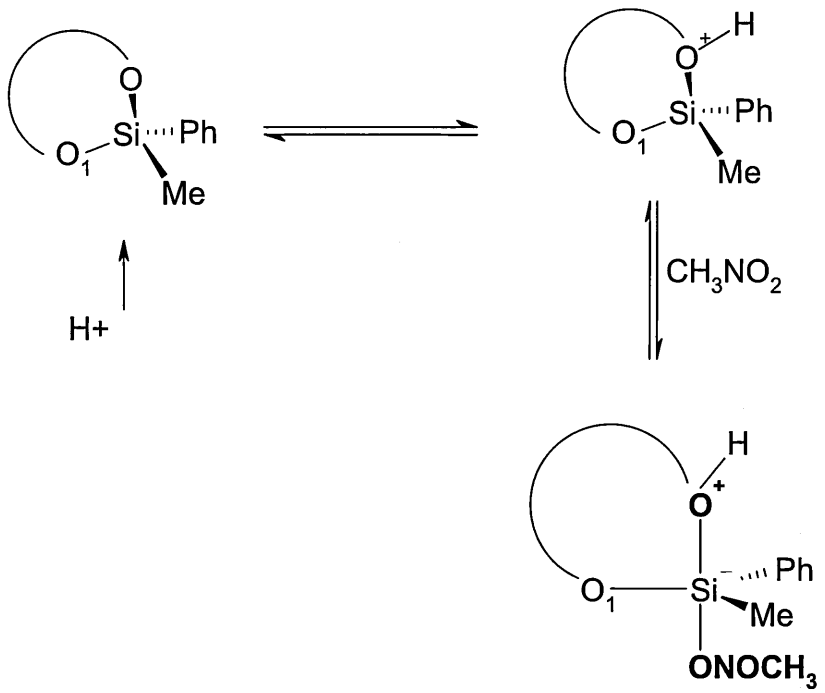


Figure 2.41 Proposed initial steps of interconversion for 2,6-*cis* in a polar aprotic solvent catalysed by triflic acid

The pentacoordinate intermediate undergoes three consecutive pseudorotations to form the interconversion products. Breaking of the silicon oxygen bond leads to polymerisation. The triflate ion is more weakly nucleophilic, compared to the methanesulphonate anion, as is the nitromethane, inducing little silicon oxygen bond breakage. The triflic acid catalysed system provides a larger window for isomerisation versus polymerisation compared to the methanesulphonic acid catalysed system. Methanesulphonate is a better nucleophile, making the pentacoordinate silicon complex less stable and observable over a smaller range.

Chojnowski et al. showed that cyclosiloxane polymerisation initiated by the super acid $Ph_3C^+B(C_6F_5)^-_4 + HSiR_3$ occurs relatively slowly because the $B(C_6F_5)^-_4$ counterion is a weak nucleophile.[124] The results suggest that these nucleophiles, or water acting as a nucleophile, attack a ring siloxane, leading to ring-opened intermediates containing a Si-

nucleophile bond. The resulting silanol group can participate in nucleophilic attack of another cyclosiloxane and propagate the polymerisation. We also observed a slow polymerisation rate with weak nucleophiles, similar to Chojnowski's results. Triflic acid produced minimal polymerisation products with approximately 1mM of catalyst, but interconversion was observed. Interconversion was even slower with the weaker methanesulphonic acid, and reasonable interconversion rates were not obtained until almost 20 mM catalyst was added. The strength of the nucleophile determines the rate of polymerisation as well as interconversion, and this may be an indication for the existence of commonalities between the polymerisation and interconversion mechanisms.

The relative rates of two competing reactions, interconversion and polymerisation, can be adjusted on the basis of catalyst choice as well as its concentration and reaction temperature. At high catalyst concentrations or high temperatures, polymerisation of 2,6-*cis* was observed in all experiments.

2.4 Summary

When low (<1 mM) concentrations of the protic catalyst triflic acid were used, the interconversion of one isomer of 2,6-diphenylhexamethylcyclotetrasiloxane to the equilibrium mixture of the two isomers occurred, provided the reaction was carried out in a polar aprotic solvent, such as nitromethane or acetonitrile. This provides the first instance of 2,6-*cis* interconversion catalysed by a protic acid. The weaker acid, methanesulphonic acid (CH_3SO_3H), required a larger concentration (20 mM) to promote interconversion, but polymerisation ensued. Brönsted acids of a strongly nucleophilic (e.g. Cl^-, HSO_4^-, etc.) conjugate base toward silicon produced ring-opened polymerisation products. When the nucleophile was weaker toward silicon (triflate or methanesulphonate), interconversion of the isomers was observed before polymerisation.

A narrow region was studied where the conditions produced a reasonable kinetic rate for the equilibrium interconversion reaction, and polymerisation followed. The preference towards ring-opening polymerisation appears to be a function of the nucleophilicity of the conjugate base of the catalysts.

Both interconversion and polymerisation reactions are first-order with respect to the cyclosiloxane reactant. First-order in triflic acid catalyst was obtained with a corrected acid concentration. The reaction can be described as $J = k\,[2,6\text{-}cis]^1[\text{triflic acid}]^1$ becoming second-order overall. A minimum concentration of catalyst ("inactive") was necessary before interconversion or polymerisation was observed, even with the use of treated vials. A portion of the acid may have been consumed by a base, possibly present in the nitromethane solvent.

A larger concentration (> 20 times) of methanesulphonic acid catalyst was necessary to impart a similar rate of interconversion versus triflic acid, and this small basic impurity would not have as significant of an impact on the larger concentrations of acid used. Polymerisation was observed with methanesulphonic acid by monitoring the change in the sum of [2,6-*cis*] and [2,6-*trans*]. Second order in catalyst was observed with methanesulphonic acid as the catalyst for both interconversion and polymerisation after subtraction of a small concentration of inactive catalyst. The reaction may be described as $J = k\,[2,6\text{-}cis]^1[\text{methanesulphonic acid}]^2$. The activation energy for the interconversion of 2,6-*cis* isomer catalysed by methanesulphonic acid was determined to be 16.0 kJ mol^{-1}, while the activation energy for polymerisation is larger, determined to be 42.4 kJ mol^{-1}. This is consistent with the observation that polymerisation is slower than interconversion.

The $\Delta S^{\ddagger}$ for all reactions was determined to be negative, and the mechanism proceeds through a more ordered transition state. It appears protonation is an important step in the interconversion reaction studied. The addition of a proton sponge, DBMP,

prevented both the interconversion and the polymerisation reactions when catalysed by triflic acid. First-order in triflic acid suggests that H^+ is involved in the transition state of the interconversion mechanism. Second-order in methanesulphonic acid for both interconversion and polymerisation suggests that both H^+ and $CH_3SO_3^-$ are involved. A common protonated pentacoordinate silicon mechanism is postulated, where the stability of the pentacoordinate silicon controls the balance between interconversion and polymerisation. A similar protonated pentacoordinate silicon species is proposed for the interconversion catalysed by triflic acid. The solvent is suggested as the nucleophile, since the order in triflic acid is first, and the triflate ion is a weaker nucleophile than the methanesulphonate.

The interconversion mechanism appears to have some similarities to the polymerisation mechanism, where protonation is a necessary step and thought to be the first step. A mechanistic scheme that encompasses interconversion and ring-opening polymerisation reactions of the 2,6-diphenylhexamethylcyclotetrasiloxanes is displayed in Figure 2.42. The mechanism for both interconversion and polymerisation of this cyclosiloxane is hypothesised to proceed through similar first two steps. Protonation of the siloxane oxygen occurs in the first step followed by nucleophilic attack of the adjacent silicon atom to form a pentacoordinated silicon.

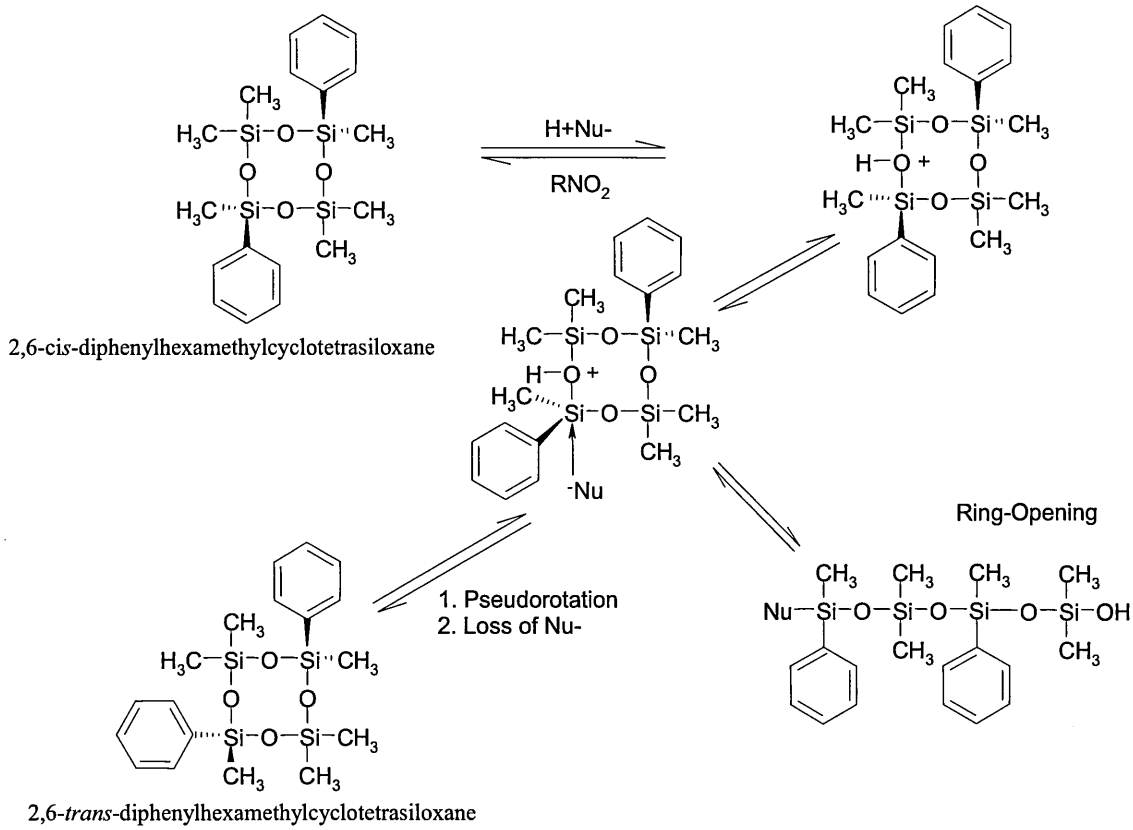


Figure 2.42 Proposed mechanism for interconversion/ polymerisation of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by a Brönsted acid in a polar aprotic solvent, where Nu is X^- (in HX) or may be solvent

Stereoisomer interconversion occurs when the pentacoordinate silicon intermediate (centre molecule in Figure 2.42) is stable or has a lifetime that allows for pseudorotation. A moderate nucleophile (e.g. methanesulphonate) will attack the silicon atom and form a pentacoordinated silicon intermediate with a long enough life time to pseudorotate. The solvent (e.g. nitromethane) may act as the nucleophile to form the pentacoordinate intermediate when the nucleophile is very weak (e.g. triflate). Silicon oxygen bond breaking and polymerisation ensue when the pentacoordinate silicon intermediate is not as stable. This is due to attack of a strong nucleophile (X^-) which leads to Si-O bond cleavage and the pentacoordinate intermediate is not long enough lived to pseudorotate.

Chapter Three

Interconversion Catalysed by Lewis Acids

3 Interconversion Catalysed by Lewis Acids

3.1 Introduction

This chapter describes the reactions of 2,6-diphenylhexamethylcyclotetrasiloxane when catalysed by iron (III) chloride (a Lewis acid). Gilbert Newton Lewis defined an acid as an electron pair acceptor and a base as an electron pair donor.[99] The proton is an acid because it contains an empty 1*s* orbital capable of accepting a pair of electrons. Protons are not the only acids, because any species capable of accepting a pair of electrons is an acid according to this definition. Thus, $AlCl_3$ serves as an acid, because the aluminium is capable of accepting a pair of electrons into its lowest unoccupied orbital. Some examples of Lewis acids are nonprotic, including metal halides such as $AlCl_3$, $SnCl_4$, BF_3, $FeCl_3$, $ZnCl_4$, etc., and derivatives such as $Al(CF_3SO_3)_3$.

We have examined two of the iron chloride catalysed reactions in which 2,6-diphenylhexamethylcyclotetrasiloxane can participate—polymerisation and interconversion. Polymerisation occurs through an acid-catalysed, ring-opening process whose detailed mechanism is not yet fully understood. The rate at which interconversion and polymerisation occurs was found to be dependent upon temperature and iron chloride catalyst concentration, as will be demonstrated. A proton sponge was used to evaluate the potential role of protons or water in the Lewis acid catalysed interconversion. The formation of a proton sponge-Lewis acid complex, which prevents the catalysis of interconversion, could not be dismissed. Only polar aprotic solvents are shown as successful mediums for interconversion.

The reactions of 2,6-*cis* in nitromethane solvent catalysed by iron (III) chloride were followed by GC and the rate of interconversion was determined. The methods used for analysis and determination of kinetic parameters were similar to those described in

Chapter 2 (Section 2.1.1). The concentration of the isomers of 2,6-diphenylhexamethyl-cyclotetrasiloxane was calculated based on a response factor to the naphthalene internal standard, according to Section 5.4. The equilibrium isomeric concentrations were, as expected, found to be approximately 1:1 2,6-*cis*:2,6-*trans*. The equilibrium isomeric product concentrations were used to define the final product mixture and to quantify the approach to equilibrium over the entire time length of the reaction. The kinetic data are contained in tables in Appendix C for reactions catalysed by iron chloride.

3.2 Comparison of 2,6-*cis* and 2,6-*trans* as the Interconversion Substrate

Strong Brönsted acids, such as common mineral acids, are used in the polymerisation and rearrangement processes for siloxanes.[4] Frye and Spielvogel showed an isomeric interconversion of a particular cyclosiloxane with a Lewis acid catalyst in a polar aprotic solvent, as discussed in Section 1.3.[80] Their goal was to enhance the *cis* isomer of 2,6-diphenylhexamethylcyclotetrasiloxane. Starting with either the 2,6-*cis* or the 2,6-*trans* isomer, an approximate equimolar mixture of isomers is obtained. A study using either 2,6-*cis* or 2,6-*trans* as the starting material in nitromethane with an iron chloride catalyst was followed by the GC method discussed above in an effort to confirm and expand their findings and to elucidate the mechanism. This analytical method is described in Section 2.1.1 in more detail. A relatively low concentration of Lewis acid was used so that the reaction rate was slow enough to obtain useful results for kinetic analyses with the methods used. Two interconversion reactions were performed, one starting with 2,6-*cis* and the other starting with 2,6-*trans*. These reactions can be followed by plotting the production of the new isomer, An example is shown in Figure 3.1 as the production of each isomer (2,6-*trans* or 2,6-*cis* respectively) with the other isomer as starting material.

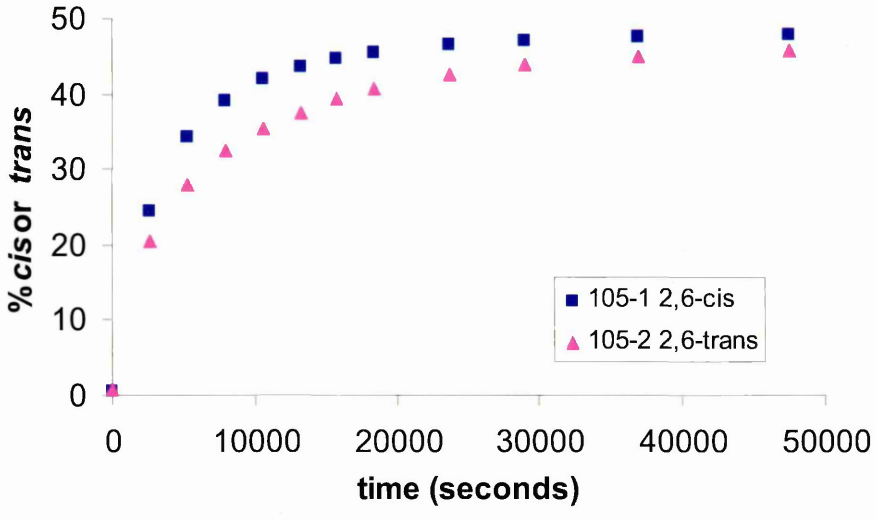


Figure 3.1 Interconversion of 2,6-diphenylhexamethylcyclotetrasiloxane (*trans* = triangles, *cis* = squares) catalysed by 0.51 mM iron chloride in nitromethane at 60°C

The tabulated GC data for these 2,6-*cis* and 2,6-*trans* comparative interconversion reactions are contained in Appendix C for the iron chloride catalysed reactions. Each reaction proceeds to a similar mixture of approximately 50:50 of the 2,6-*cis*:2,6-*trans* isomers, as was observed with the Brönsted acid catalysed interconversion. The 2,4-isomers were not observed in the gas chromatogram. The presence of 2,4-isomers would indicate ring-opening at more than one bond followed by ring-closure.

The interconversion reaction obeys first-order kinetics. A similar rate constant for the interconversion reaction is evident (Figure 3.2) when either isomer (2,6-*cis*, or 2,6-*trans*) was used as the starting material.

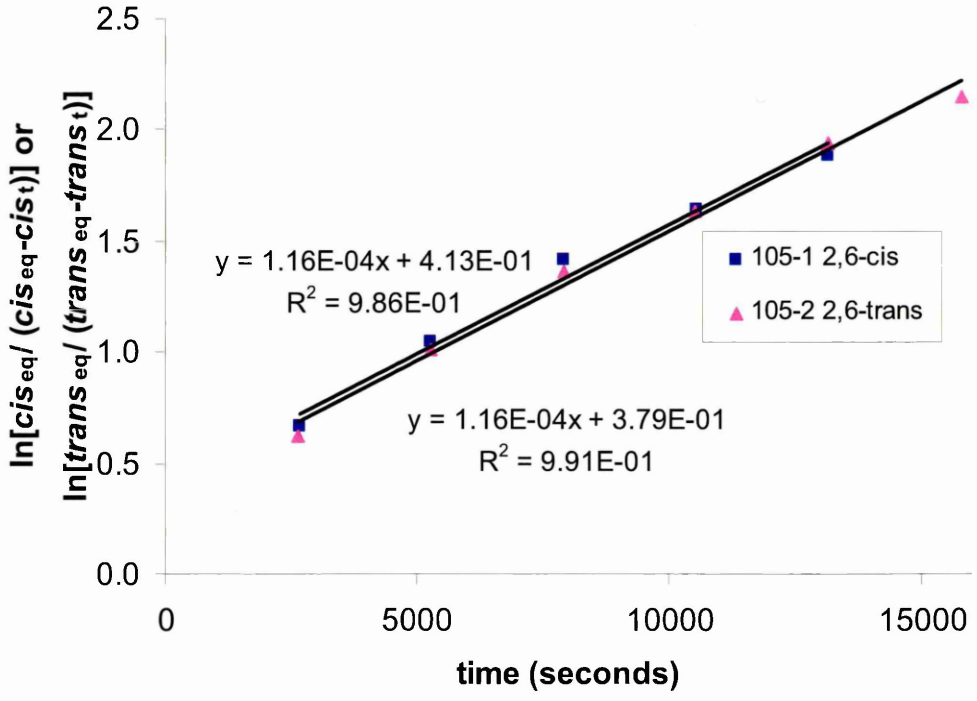


Figure 3.2 First order plot for the interconversion of 2,6-diphenylhexamethyl-cyclotetrasiloxane (*trans* = triangles, *cis* = squares) catalysed by 0.51 mM of iron chloride in nitromethane at 60°C

The production of the other stereoisomer for the two separate interconversion reactions is shown in Figure 3.2 (e.g., a plot of the production of 2,6-*cis* is shown for the 2,6-*trans* starting material reaction). The linearity of the ln [isomer] versus time data for each of the two reactions represented in Figure 3.2 suggests that this interconversion is indeed first-order in 2,6-diphenylhexamethylcyclotetrasiloxane. The rate constant thus found for the reaction of 2,6-*cis* to an approximate equimolar mixture of 2,6-*cis* and 2,6-*trans* is 1.16×10^{-4} s^{-1}, from the slope in Figure 3.2. The rate constant for the reaction of 2,6-*trans* is also 1.16×10^{-4} s^{-1}. The production of a similar 2,6-diphenylhexamethylcyclotetrasiloxane isomeric mixture was observed from the interconversion reaction when either *cis* or *trans* isomer was used as the reactant. The interconversion reaction of either isomer results in first-order with respect to the siloxane starting material, when catalysed by iron chloride. This supports the findings of Frye and

Spielvogel, where Lewis acids catalyse the interconversion without interference from polymerisation in a polar aprotic solvent.

3.3 Evaluation of Iron Chloride Catalysed Interconversion

As discussed in Section 3.2, the interconversion reaction of 2,6-*cis* or 2,6-*trans* with iron chloride in nitromethane obeys a first-order kinetic law with respect to the starting material. Similar first-order results were observed for the interconversion reaction of 2,6-*cis* catalysed by triflic acid, see Section 2.3.2. A more detailed analysis of 2,6-*cis* catalysed by iron chloride follows, in order to more directly compare the kinetics of interconversion catalysed by Lewis acids with those using Brönsted acids.

The effect of temperature on the rate of interconversion of 2,6-*cis* was evaluated at two concentrations (0.76 mM and 0.51 mM) of iron chloride catalyst at 40, 50, 60, and 70°C using the same GC method outlined for the triflic acid catalysed reactions in Section 2.1.1. Naphthalene was again used as the internal standard. The reaction proceeded to the 49.8:50.2 equilibrium of 2,6-*cis* :2,6-*trans* as observed with the Brönsted acid catalysed interconversion reactions studied in Chapter 2. The rate constants for each catalyst concentration conducted at the same temperature were calculated according to first-order kinetics while using the equivalent concentration of the siloxane starting material. The results from following the loss of the [2,6-*cis*] isomer in nitromethane at 40°C (Figure 3.3) represents 80% reaction completion.

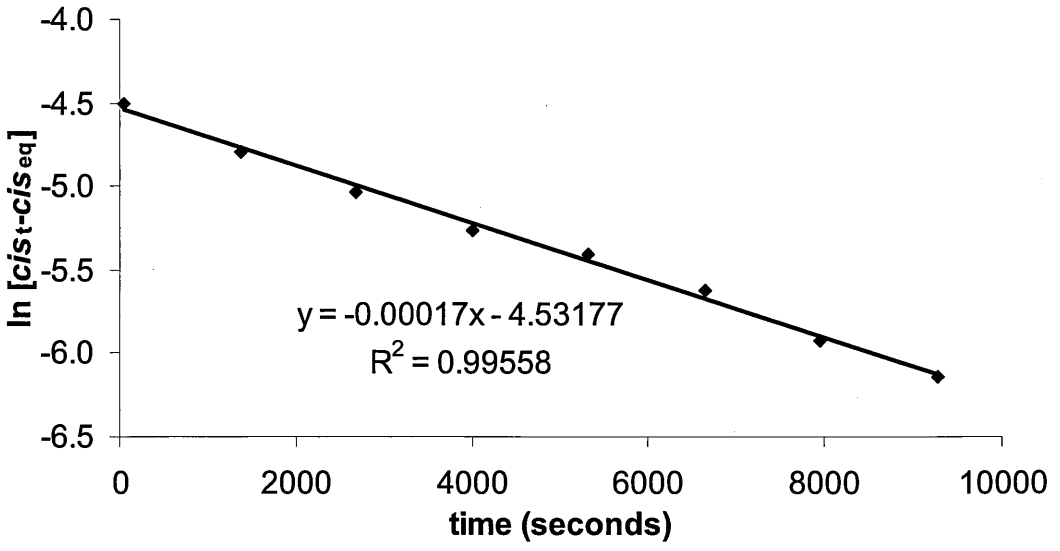


Figure 3.3 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM iron chloride in nitromethane at 40°C, where the GC data show the loss of the [2,6-*cis*] isomer

The rate constant at which 2,6-*cis* was lost (1.7×10^{-4} s^{-1} from Figure 3.3) equates, within experimental error, to that obtained from the production of the 2,6-*trans* isomer (1.7×10^{-4} s^{-1}, in Figure 3.4) indicating no polymerisation. This shows minimal side reactions have taken place in this single experiment, where as Figure 3.2 showed two experiments with different starting materials (2,6-*cis* or 2,6-*trans*) proceeding at a similar rate constant to a similar equilibrium mixture of isomeric products.

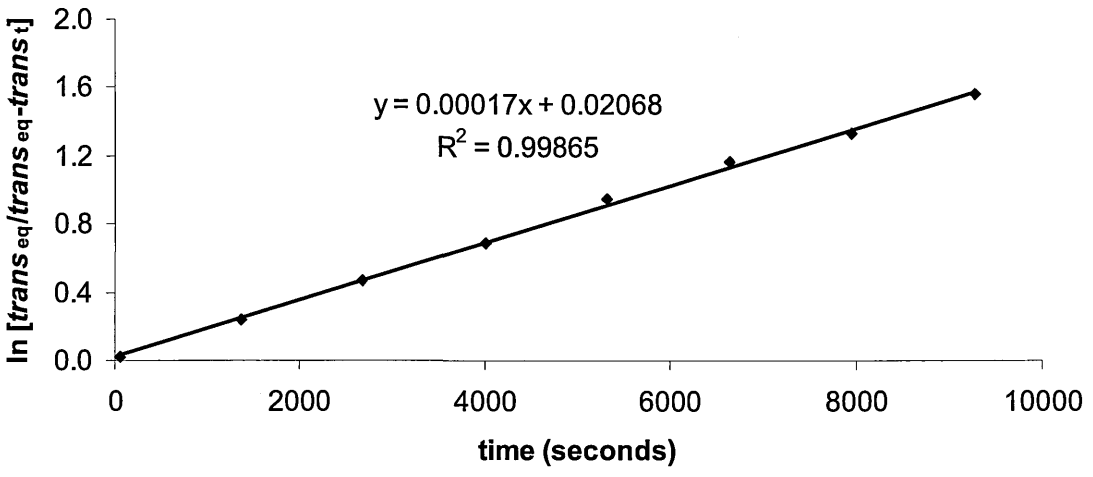


Figure 3.4 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM iron chloride in nitromethane at 40°C, where the GC data show the production of the [2,6-*trans*] isomer

The GC data and corresponding isomer concentrations are contained in Appendix C for the interconversion reaction based on the production of the 2,6-*trans* isomer and the loss of the 2,6-*cis* isomer, along with the first-order plots. The rate constants obtained from these data over the 40 to 70°C range for interconversion catalysed by iron chloride are summarised in Table 3.1.

$FeCl_3$ (M)	Temperature	Sample	*k* (-loss of 2,6-*cis*) (1/sec)	*k* (production of 2,6-*trans*) (1/sec)
7.6E-04	70°C	88	1.11E-03	1.04E-03
	60°C	90	6.70E-04	7.00E-04
	50°C	92	3.90E-04	3.80E-04
	40°C	94-1	1.70E-04	1.70E-04
5.1E-04	70°C	89	5.40E-04	5.20E-04
	60°C	91	3.00E-04	3.00E-04
	50°C	93-1	1.34E-04	1.29E-04
	40°C	94-2	6.00E-05	6.00E-05

Table 3.1 Rate constants for the interconversion reactions of 2,6-*cis*-diphenyl-hexamethylcyclotetrasiloxane catalysed by iron chloride in nitromethane at various temperatures

The interconversion data appear to follow the generic kinetic guideline of the rate

doubling for every 10°C rise in temperature. The GC data for the loss of 2,6-*cis* and the production of 2,6-*trans* data show the same rate constants, within the experimental error.

As observed with the Brönsted acid, triflic acid, a minimum concentration of catalyst was required before product was observed on the time scale of the reaction. These experiments preceded the confirmation in Chapter 2 that without GC vial treatment a reduction in the rate constant was observed. All of the experiments in this chapter (Chapter 3) were carried out with untreated vials. The concentration of inactive catalyst in the system was determined from the results in Table 3.1, where a minimum concentration of catalyst was required before the rate constant would be above zero. A plot of the rate constant (k) versus the concentration of acid at each temperature produced a line when the order in catalyst is first order. The extrapolated x-intercept of this line represents the concentration of inactive catalyst, shown in Table 3.2.

Sample	$FeCl_3$ (mol/L)	k (-loss of cis)	x-intercept (mol/L)
70°C			
88	7.61E-04	1.1E-03	2.7E-04
89	5.07E-04	5.4E-04	
60°C			
90	7.61E-04	6.7E-04	3.2E-04
91	5.07E-04	3.0E-04	
50°C			
92	7.61E-04	3.9E-04	3.8E-04
93-1	5.07E-04	1.3E-04	
40°C			
94-1	7.61E-04	1.7E-04	3.7E-04
94-2	5.07E-04	6.0E-05	

Table 3.2 Inactive catalyst concentration calculated for the interconversion reactions of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by iron chloride in nitromethane at various temperatures

This method indicates 0.37 mM, 0.38 mM, 0.32 mM, and 0.27 mM iron chloride that was inactive for interconversion at 40, 50, 60, and 70°C, respectively. The confidence

level of the inactive catalyst is somewhat low due to the equation of the line being based only on two data points (two catalyst concentrations), but it does provide at least some representation of the concentration of inactive catalyst in this system. Similar results were obtained when the interconversion reaction was analysed for the inactive catalyst concentration calculation from GC data of the production of 2,6-*trans* isomer. The corrected catalyst concentration is the initial acid concentration placed into the system minus the concentration of inactive catalyst calculated from the GC data of loss of 2,6-*cis*. The corrected acid concentration and corresponding natural logarithms for the Arrhenius plot are listed in Table 3.3.

$FeCl_3$ (M)	Temperature	Sample	*k* (-loss of2,6-*cis*) (1/sec)	*k* (production of 2,6-*trans*) (1/sec)	$[FeCl_3]$ (M) (corrected)	ln $[FeCl_3]$ (corrected)
7.61E-04	**70°C**	88	1.1E-03	1.0E-03	4.9E-04	-7.62
	60°C	90	6.7E-04	7.0E-04	4.4E-04	-7.73
	50°C	92	3.9E-04	3.8E-04	3.8E-04	-7.87
	40°C	94-1	1.7E-04	1.7E-04	3.9E-04	-7.85
5.07E-04	**70°C**	89	5.4E-04	5.2E-04	2.4E-04	-8.35
	60°C	91	3.0E-04	3.0E-04	1.9E-04	-8.58
	50°C	93-1	1.3E-04	1.3E-04	1.3E-04	-8.97
	40°C	94-2	6.0E-05	6.0E-05	1.4E-04	-8.89

Table 3.3 Rate constants for the interconversion reaction of 2,6-*cis*-diphenyl-hexamethylcyclotetrasiloxane catalysed by two concentrations of iron chloride in nitromethane at various temperatures, including corrected [acid]

A portion of the iron chloride has been deactivated. This is similar to the triflic acid catalysed interconversion, where the consumption of catalyst was presumed due to the presence of a basic impurity. The dilution of iron chloride catalyst in nitromethane, which was used to dissolve the solid catalyst, produced a yellow solution. The glass GC sample vials used for the interconversion reactions in this chapter (Chapter 3) were not treated to reduce residual moisture, as these experiments were performed prior to the vial treatment study discussed in Chapter 2 (Section 2.1.2.4). Karl Fischer titration was used to determine that 50 ppm of water was present in the nitromethane solvent (Section 5.3),

which increased to 132 ppm with the addition of iron chloride to the solvent.

Several factors may be contributing to the formation of inactive catalyst. Schlogel and Jones studied crystalline iron chloride using X-ray diffraction and Mossbauer spectra from a standard constant-acceleration spectrometer.[125] They found that direct exposure of crystalline iron chloride to air resulted in the rapid formation of a yellow liquid which contained hydrogen chloride. A brown precipitate was formed within 24 hours. The yellow liquid was postulated to contain FeO(OH), FeOCl, and residual $[FeCl_4]^-$ based on Mossbauer spectroscopy. The iron chloride catalyst dilutions used for the interconversion reactions were yellow in colour and some precipitate was observed. This is an indication of the presence of moisture in the system, which is supported by the Karl Fischer data.

A minor basic impurity in the solvent would easily consume the acid catalyst, as the catalyst concentrations studied are small (1 mM). In Chapter 2, we postulate that the nitromethane solvent contains a small amount of a basic impurity, possibly an amine (RNH_2). The presence of water, or a base in the system, is a possible cause of the apparent reduced activity of the iron chloride in our interconversion reactions.

The data in Table 3.3 can be used to determine the order of the reaction by comparing the logarithm of the rate constant versus the logarithm of the catalyst concentration. The slope of the line provided the order in catalyst for the interconversion reaction. The order was determined as a function of temperature between the 40 to 70°C range. Although based on very limited data (two catalyst concentration data points at each temperature), the reaction order with respect to catalyst was determined to be consistently near first order using the corrected catalyst concentrations, where 1.00, 0.97, 0.94, and 0.99 was obtained for 40, 50, 60, and 70°C respectively. Similar results (0.95 to 1.00) were obtained when following the production of 2,6-*trans* isomer.

The confidence that these data are first-order in catalyst is enhanced based on data

obtained early in the project. Interconversion of 2,6-*cis* in nitromethane was analysed by the same GC method discussed above when catalysed by iron chloride at room temperature. The original GC data has been lost, but Table 3.4 contains the concentrations and resulting rate constants for the samples studied.

Sample	$FeCl_3$ (mol/L)	$FeCl_3$ (mol/L) (corrected)	2,6-cis (mol/L)	*k* (sec^{-1})
71-6	1.47E-03	9.07E-04	0.0305	9.38E-06
71-7	1.96E-03	1.40E-03	0.0305	1.51E-05
71-8	2.44E-03	1.89E-03	0.0305	2.05E-05
67-4	1.33E-03	7.75E-04	0.0339	7.40E-06
67-5	1.78E-03	1.22E-03	0.0339	1.28E-05
67-6	2.22E-03	1.66E-03	0.0339	1.74E-05
67-1	8.89E-04	3.30E-04	0.0339	4.69E-06
67-2	8.89E-04	3.30E-04	0.0509	3.03E-06
67-3	8.89E-04	3.30E-04	0.0679	3.61E-06

Table 3.4 Rate constants for the interconversion reactions of 2,6-*cis*-diphenyl-hexamethylcyclotetrasiloxane catalysed by iron chloride in nitromethane at room temperature

The rate constants were best described by first-order kinetics. The impact the catalyst concentration has on the rate constant is shown in Figure 3.5.

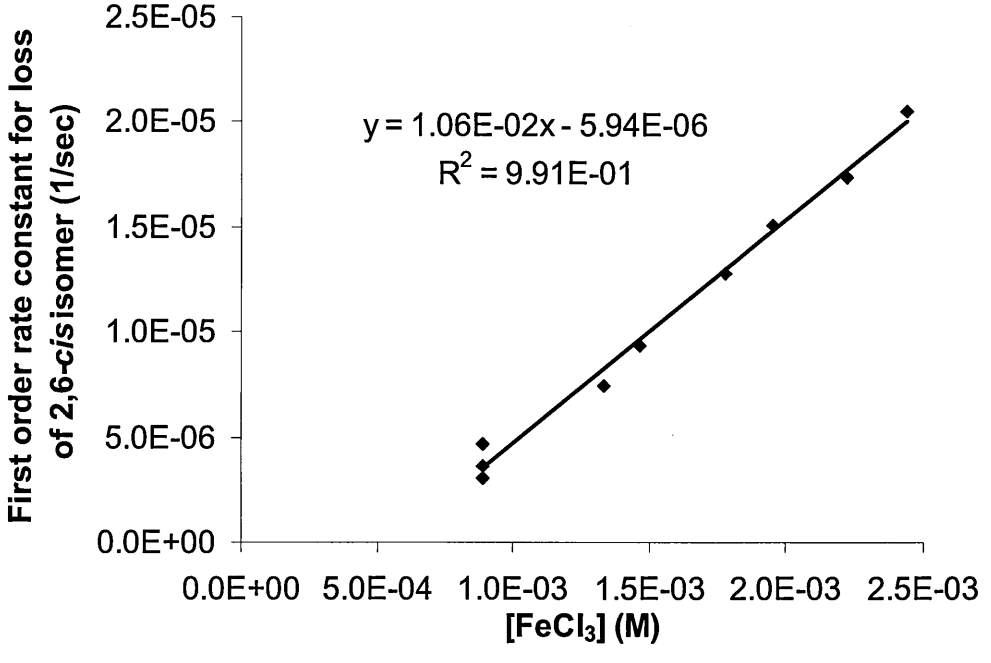


Figure 3.5 Rate constant versus concentration of iron chloride for 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of iron chloride in nitromethane at room temperature.

A correction factor of 5.59 x 10^{-4} M is calculated from the *x*-intercept of the best fit line to the data in Figure 3.5. This "inactive" catalyst concentration is subtracted from the initially added catalyst concentration (Table 3.5).

Sample	$FeCl_3$ (mol/L)	$FeCl_3$ (mol/L) (corrected)	2,6-cis (mol/L)	*k* (sec^{-1})	ln [$FeCl_3$] (corrected)	ln *k*
71-6	1.47E-03	9.07E-04	0.0305	9.38E-06	-7.01	-11.58
71-7	1.96E-03	1.40E-03	0.0305	1.51E-05	-6.57	-11.10
71-8	2.44E-03	1.89E-03	0.0305	2.05E-05	-6.27	-10.79
67-4	1.33E-03	7.75E-04	0.0339	7.40E-06	-7.16	-11.81
67-5	1.78E-03	1.22E-03	0.0339	1.28E-05	-6.71	-11.27
67-6	2.22E-03	1.66E-03	0.0339	1.74E-05	-6.40	-10.96
67-1	8.89E-04	3.30E-04	0.0339	4.69E-06	-8.02	-12.27
67-2	8.89E-04	3.30E-04	0.0509	3.03E-06	-8.02	-12.71
67-3	8.89E-04	3.30E-04	0.0679	3.61E-06	-8.02	-12.53

Table 3.5 Rate constants for the interconversion reaction of 2,6-*cis*-diphenyl-hexamethylcyclotetrasiloxane catalysed by various concentrations of iron chloride in nitromethane at room temperatures, including corrected [acid]

The data in Table 3.5 can be used to determine the order of the reaction by comparing the logarithm of the rate constant versus the logarithm of the catalyst concentration. The slope of the line provided the order in catalyst for the interconversion reaction (Figure 3.6).

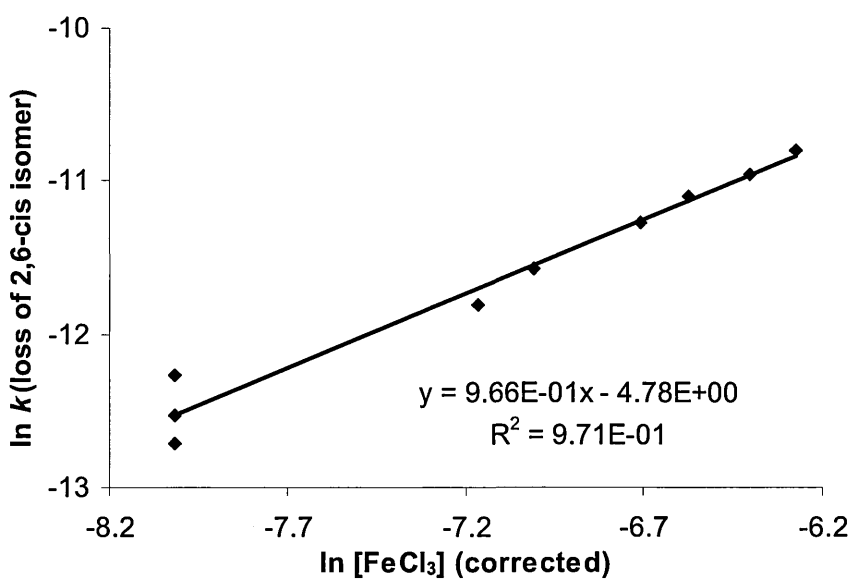
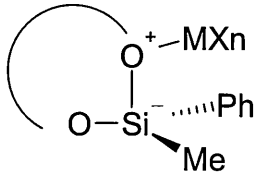
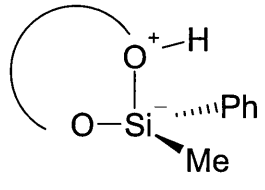


Figure 3.6 Interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by various concentrations of iron chloride (corrected) in nitromethane at room temperature

The slope of the linear fit in Figure 3.6 is 0.97 for the rate constant at room temperature, indicating that first-order kinetics best describe the interconversion reaction catalysed by iron chloride at room temperature. These data served as a basis for the first-order results for interconversion obtained above from two catalyst concentration data points.

First order in catalyst suggests one molecule of catalyst participates in the rate determining step of the reaction. The iron chloride may complex with the oxygen in the cyclosiloxane. This metalated complex or a protonated oxygen complex would weaken the neighbouring silicon-oxygen bond, causing the silicon to be susceptible to nucleophilic attack. Protonation of the cyclosiloxane oxygen was proposed as the first step with triflic and methanesulphonic acid catalysed interconversion. The water present in the iron chloride system could provide the proton, possibly through a super acid formed by reaction of water and iron chloride.





As with triflic acid, the nucleophile for the iron chloride catalysed interconversion may be the solvent, since it is, by comparison with others, nucleophilic and is in excess. A similar pentacoordinate intermediate is proposed. Based on the discussion in Chapter 2, this pentacoordinate silicon intermediate is stable enough to undergo pseudorotations (Figure 3.7), which accounts for the observance of only interconversion products.

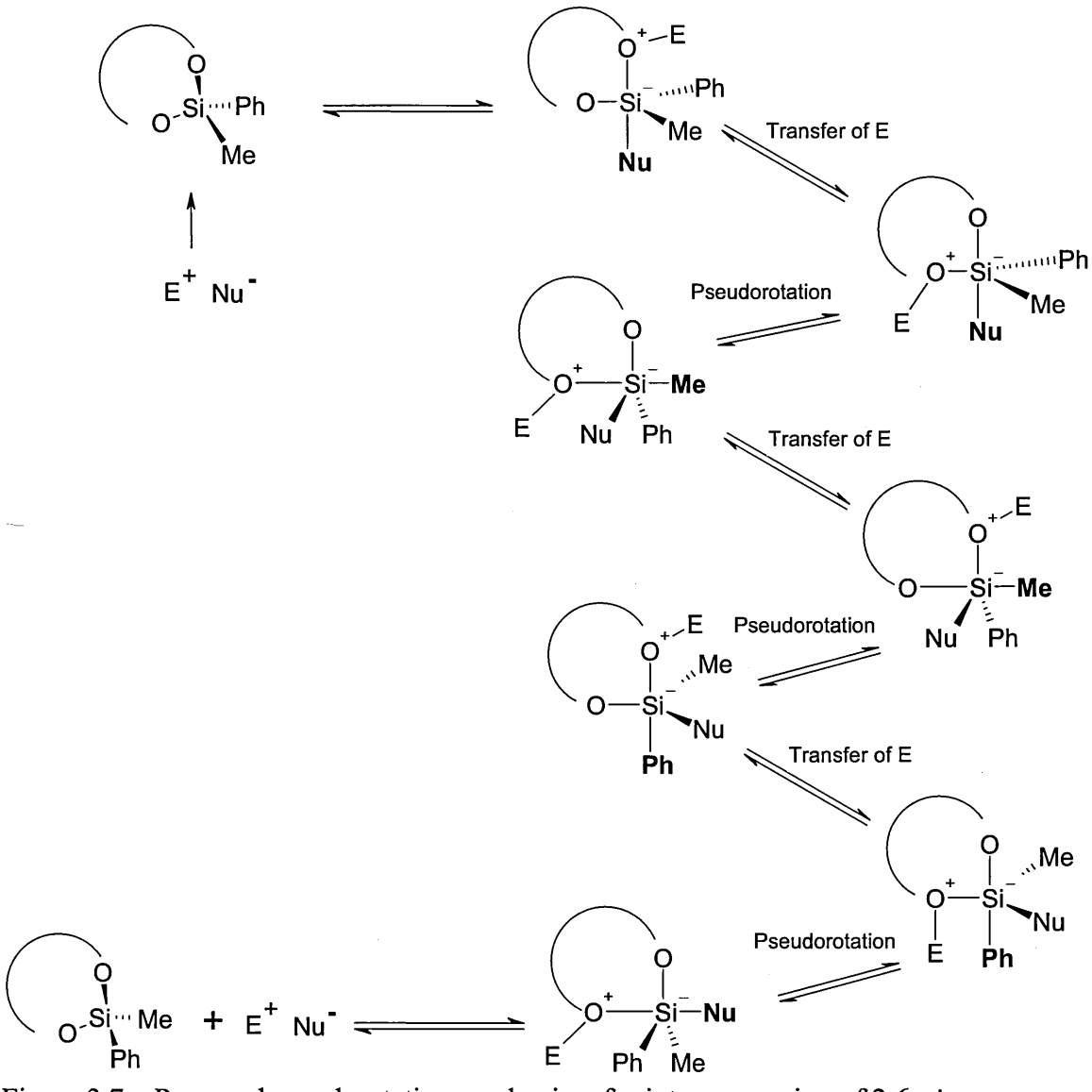


Figure 3.7 Proposed pseudorotation mechanism for interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane in a polar aprotic solvent (E= H, or metal complex)

The data points necessary for an Arrhenius plot and their corresponding acid concentrations for the rate constants using the loss of 2,6-*cis* are displayed in Table 3.6. (These are the same rate constants from Table 3.1.)

Temp (K)	313	323	333	343
[$FeCl_3$] (M)	7.6E-04	7.6E-04	7.6E-04	7.6E-04
[$FeCl_3$] (M) (corrected)	3.9E-04	3.9E-04	4.4E-04	4.9E-04
k (-loss of 2,6-*cis*) (1/ sec)	1.7E-04	3.9E-04	6.7E-04	1.1E-03
1/Temp (1/K)	0.0032	0.0031	0.0030	0.0029
ln *k*	-8.68	-7.85	-7.31	-6.80
ln (*k*/*T*)	-14.4	-13.6	-13.1	-12.6

Temp (K)	313	323	333	343
[$FeCl_3$] (M)	5.1E-04	5.1E-04	5.1E-04	5.1E-04
[$FeCl_3$] (M) (corrected)	1.4E-04	1.4E-04	1.9E-04	2.4E-04
k (-loss of 2,6-*cis*) (1/ sec)	6.0E-05	1.3E-04	3.0E-04	5.4E-04
1/Temp (1/K)	0.0032	0.0031	0.0030	0.0029
ln *k*	-9.72	-8.92	-8.11	-7.52
ln (*k*/*T*)	-15.5	-14.7	-13.9	-13.4

Table 3.6 Interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by two concentrations of iron chloride in nitromethane at various temperatures, loss of 2,6-*cis* isomer

The activation energy, E_a, and the Arrhenius constant, A, are obtained from the Arrhenius plot (Figure 3.8) interconversion reaction according to the loss of 2,6-*cis* data as described in Section 1.4.1.

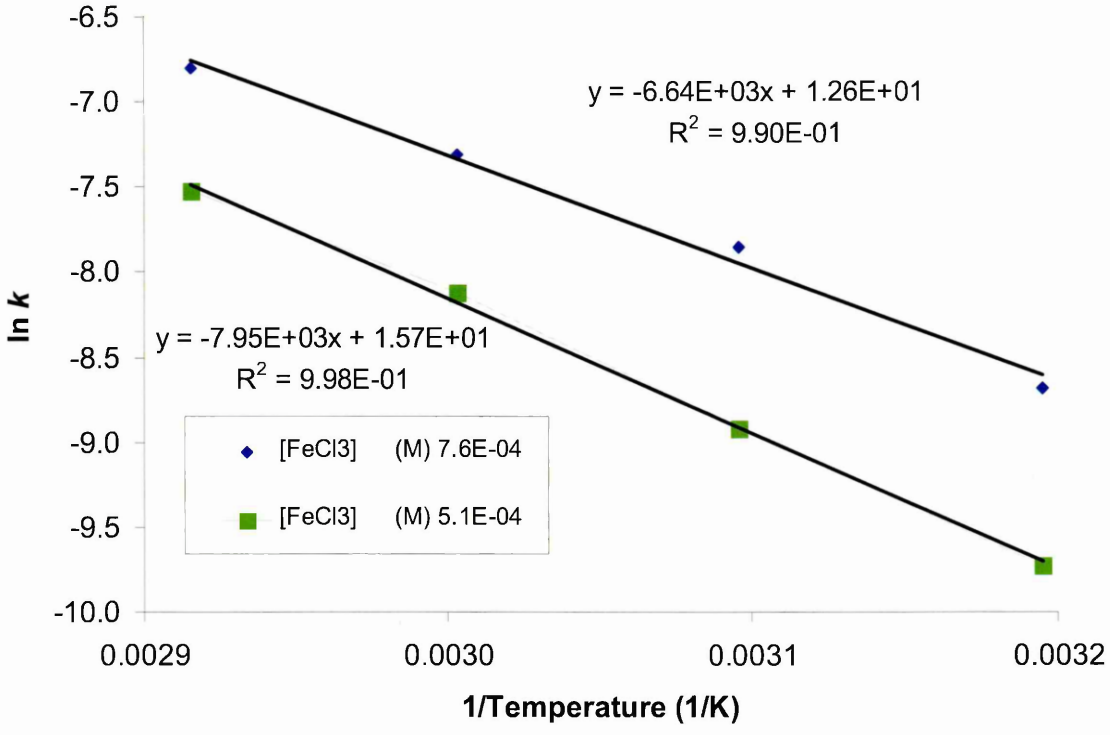


Figure 3.8 Arrhenius plot for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane based on the loss of 2,6-*cis* isomer when catalysed by two concentrations of iron chloride in nitromethane at various temperatures

According to Figure 3.8 the following values are calculated for E_a and A based on GC data for the loss of 2,6-*cis* for the interconversion reaction catalysed by 0.76 mM iron chloride and 0.51 mM iron chloride (Table 3.7).

$FeCl_3$	$FeCl_3$ (corrected)	E_a	A
0.76 mM	0.43 mM	55.2 kJ/mol (±7.0%)	3.0×10^5 (±11.2%)
0.51 mM	0.19 mM	66.1 kJ/mol (±3.4%)	6.6×10^6 (±5.3%)

Table 3.7 Activation energy (E_a) and Arrhenius parameter (A) for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by two concentrations of iron chloride according to the loss of 2,6-*cis* isomer

These activation energy results are similar to those calculated for the interconversion reaction catalysed by triflic acid and methanesulphonic acid in Chapter 2. Figure 3.9 contains the Eyring plot for the interconversion reaction of 2,6-*cis* catalysed by iron chloride.

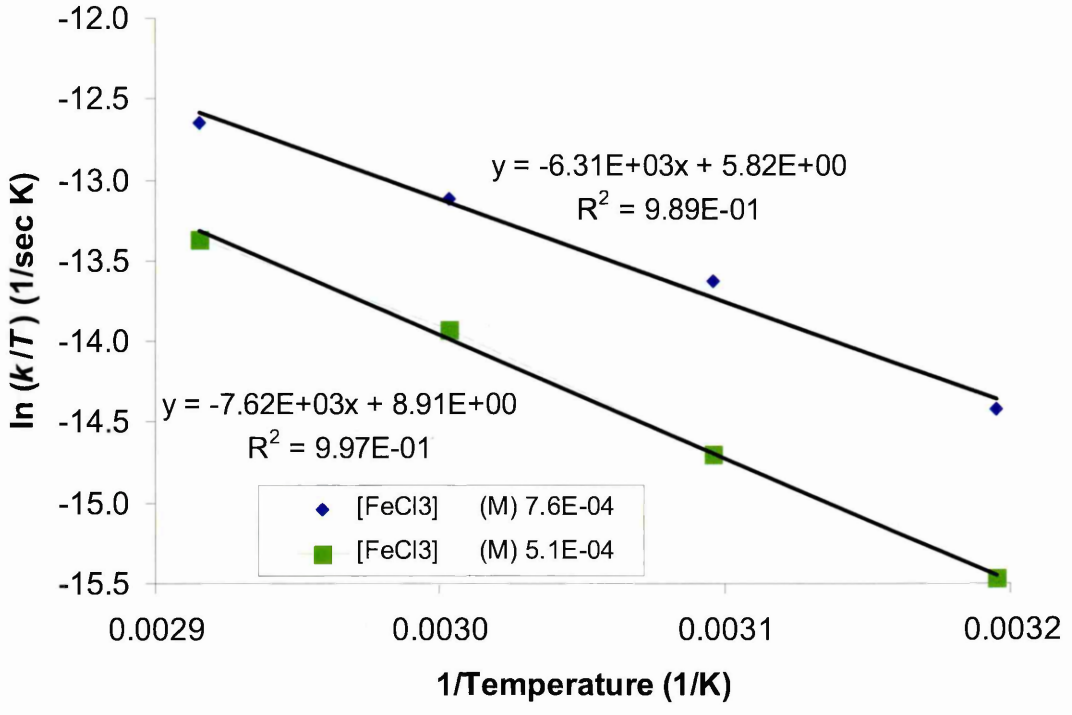


Figure 3.9 Eyring plot for the interconversion reaction of 2,6-*cis*-diphenylhexamethyl-cyclotetrasiloxane based on the loss of 2,6-*cis* isomer when catalysed by two concentrations of iron chloride in nitromethane at various temperatures

The resulting enthalpy of activation, $\Delta H^{\ddagger}$, and entropy of activation, $\Delta S^{\ddagger}$, from the interconversion reaction catalysed by 0.76 mM iron chloride and 0.51 mM iron chloride following the loss of 2,6-*cis* are shown in Table 3.8.

$FeCl_3$	$FeCl_3$ (corrected)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
0.76 mM	0.43 mM	52.5 kJ/mol (±7.4%)	-149 J/mol K (±24.5%)
0.51 mM	0.19 mM	63.4 kJ/mol (±3.6%)	-123 J/mol K (±9.4%)

Table 3.8 The standard enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) for the interconversion reaction of 2,6-cis-diphenylhexamethylcyclotetrasiloxane catalysed by two concentrations of iron chloride according to the loss of 2,6-*cis* isomer

The enthalpy of activation $\Delta H^{\ddagger}$ for iron chloride is approximately three times larger than that obtained from the interconversion reaction of 2,6-*cis* catalysed by triflic acid. Interconversion catalysed by both iron chloride and triflic acid results in a negative entropy, which implies order is induced in both systems between the starting materials and

the transition state. The entropy of activation $\Delta S^{\ddagger}$ is almost half of that obtained with triflic acid ($\Delta S^{\ddagger}$ = -253 J/mol K).

Interconversion of 2,6-*cis* or 2,6-*trans* was shown to occur with nonprotic Lewis acids, for example (<1 mM) iron chloride, in a manner similar to the results obtained with triflic acid. No interconversion was observed without a catalyst under the attempted conditions, within the time scale studied. Complexation (protonation or metal complex) of the siloxane oxygen was proposed as the first step of the interconversion reaction when catalysed by triflic and methanesulphonic acids. It is unclear whether iron chloride is acting as a Lewis acid and forming a metal complex with the siloxane oxygen or as a protic acid (or super acid) and just protonating the oxygen.

Corriu has proposed an alternative mechanism for nucleophilic attack at silicon.[126] The first step involves nucleophilic attack of the silicon to form a pentacoordinate intermediate as in the above mechanism. A second nucleophile then attacks the pentacoordinate molecule in the second step to form a hexacoordinate complex (Figure 3.10).

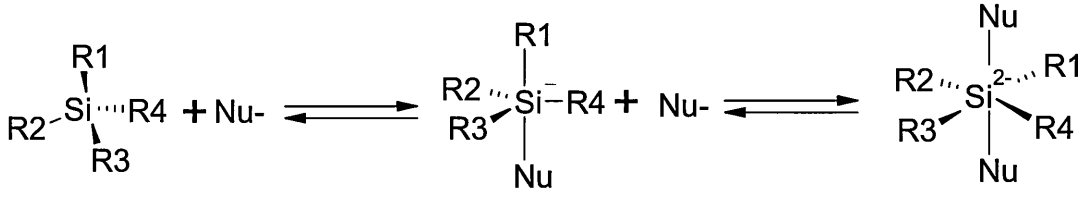


Figure 3.10 Proposed mechanism for racemisation through a hexacoordinated silicon species by Corriu

Addition of a second nucleophile that would form the hexacoordinated silicon by attack on the pentacoordinate silicon intermediate may appear improbable, particularly due to the steric hindrance and anion-anion repulsion. Although, Dieters and Holmes showed through calculations that pentacoordinated silicon species can be more reactive than the tetracoordinate counterpart.[127] This supports Corriu's second nucleophilic attack on a

pentacoordinate silicon. Second order kinetics in nucleophile is necessary for Corriu's mechanism. Second order in catalyst was only observed with methanesulphonic acid in the interconversion of 2,6-*cis*. This was used to explain protonation followed by nucleophilic attack of the methanesulphonate anion. Corriu's mechanism requires two nucleophiles, which would be third order in catalyst for a protonation mechanism. If the nucleophiles are the solvent, then the order in catalyst could be one to account for protonation. Racemisation *via* Corriu's hexacoordinate species which is second order in nucleophile must be considered, but is not consistent with the kinetic results from interconversion catalysed by Lewis and Brönsted acids, in the case studied herein.

3.3.1 Other Lewis Acids

Iron chloride was chosen as the catalyst for the above in-depth analysis of the reaction because the interconversion occurred at a rate that provided a reasonable quantity of data with this Lewis acid catalyst. Iron chloride is highly soluble in a wide array of solvents, including the polar aprotic nitromethane. A drawback to the iron chloride catalyst is its susceptibility to moisture. Lewis acids other than iron chloride were used as catalysts for the interconversion reaction of 2,6-*cis*. Zinc chloride ($ZnCl_2$) was shown to also operate as a catalyst for this interconversion without the interference of polymerisation, although at slower rates than with similar concentrations of iron chloride. Zinc chloride is not as soluble in nitromethane as iron chloride and is difficult to dry. The zinc chloride used in this study was heated under vacuum to remove moisture before use.

Lanthanum triflate and ytterbium (III) triflate were considered as catalysts for the interconversion reaction based on the work of Kobayaski et al. regarding their recent success with water tolerant Lewis acids.[77, 78] Unfortunately, the poor solubility of these Lewis acids in the polar aprotic medium nitromethane hampered their evaluation as

interconversion catalysts.

Aluminium trifluoromethane sulphonate ($Al(OSO_2CF_3)_3$) acid was evaluated as a catalyst for the interconversion reaction due to its source of three triflate anions and lack of protons compared to triflic acid. Interconversion catalysed by aluminium triflate is discussed further in Section 3.4.1.

3.4 Effect of Water

The impact of water on the reactivity of Lewis acids, iron chloride in particular, was studied. This was undertaken in order to further understand the inactive portion of catalyst that was observed in Section 3.2 and the function of water in the mechanism of interconversion.

The role of water is important because it has been reported that dry Lewis acids do not catalyse the polymerisation of cyclosiloxanes (Section 1.3.3).[69] Kendrick has shown that neither anhydrous ferric chloride nor anhydrous HCl catalyse the polymerisation of D_4 (octamethylcyclotetrasiloxane).[69] No polymerisation of 1.17 M D_4 in toluene containing 5% nitrobenzene was observed over eight months at 30°C with either 2.5×10^{-4} M ferric chloride or 4.9×10^{-3} M hydrogen chloride. Kendrick does not offer an explanation for the lack of polymerisation, mentioning only that protonation is necessary. Water-complexed Lewis acids have been shown to catalyse polymerisation by forming a Brönsted acid-like Lewis acid-water complex. The reaction of water with a Lewis acid such as iron chloride produces a protic acid capable of catalysing ring-opening polymerisation. The polymerisation of cyclosiloxanes is catalysed by a combination of hydrogen chloride and iron chloride, but the active catalyst resembles a protic acid, $H^+[FeCl_4HFeCl_4]^-$.[128]

The concentration of water present in the interconversion system was determined by Karl Fischer titration (see Section 5.3 for method details). The nitromethane solvent

contained approximately 50 ± 5 ppm of water. The dissolution of small amounts of siloxane in nitromethane did not alter this 50 ppm value, which indicates that the siloxane did not bring significant amounts of water with it. The interconversion reaction of 2,6-*cis* catalysed by iron chloride in nitromethane solvent was evaluated as a function of water concentration. Samples were prepared by dissolving 2,6-*cis* in nitromethane using untreated GC vials, and analysed according to the same technique as discussed in Section 3.2. Three of these samples contained a similar concentration of iron chloride catalyst. The fourth sample (122-4) did not contain any catalyst, and as expected, no reaction was observed. This shows that over the timeframe studied no appreciable amount of interconversion was observed without the iron chloride catalyst. The other two samples were spiked with additional water (90 and 170 ppm) for a total of 140 and 220 ppm water, respectively. The conversion from 2,6-*cis* to a mixture of 2,6-*cis* and 2,6-*trans* isomers was followed by observing the production of 2,6-*trans* by GC and is depicted in Figure 3.11.

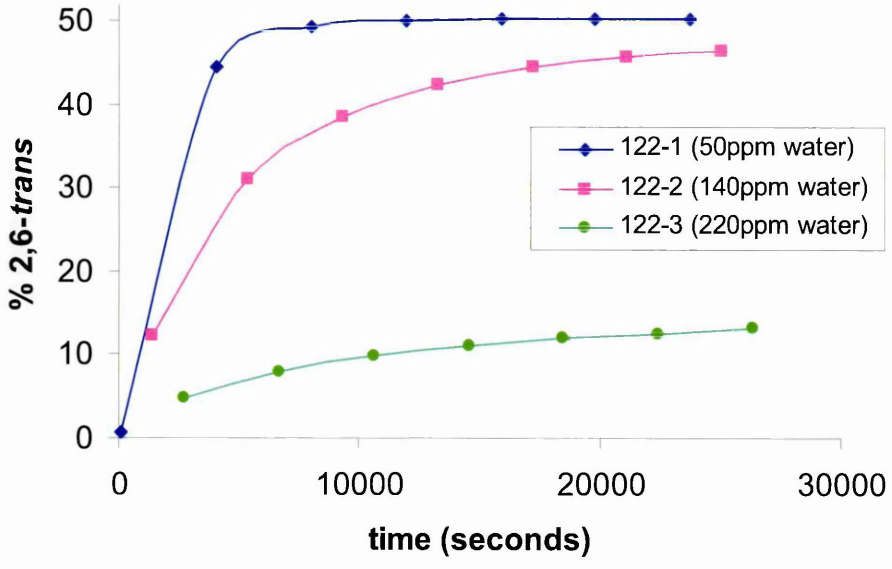


Figure 3.11 Production of 2,6-*trans* isomer from interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.71 mM iron chloride with various concentrations of water in nitromethane at 60°C

The addition of water slows the rate of product formation and may even prevent the reaction from achieving completion, as shown in Figure 3.11. The detailed GC data are contained in Appendix C. The inherent (50 ppm) amount of water in the nitromethane solvent corresponds to 3.1 mM water (assuming the solution has the same 1.127 g/ml density as nitromethane), which is four times the concentration (0.71 mM iron chloride) of catalyst in the system (122-1). Thus, even ambient water levels were above stoichiometric catalyst levels. The samples with additional water (122-2, and 122-3) contained the same concentration of catalyst (0.71 mM iron chloride), but the total concentration of water was even higher after including the water inherent in the solvent, at 8.8 mM and 13.8 mM water for samples 122-2 and 122-3, respectively. A considerable excess of water was found to be necessary to prevent the interconversion reaction.

The excess water in the system did not appear to produce Brönsted acids in concentrations capable of siloxane ring-opening, i.e. polymerisation. The [*cis*] + [*trans*] amount was relatively constant over the time period studied (see Figure 3.12). If

compounds other than the interconverted cyclosiloxanes 2,6-*cis* and 2,6-*trans* were produced, the sum of [*cis*] + [*trans*] (Figure 3.12) would decrease as other products formed. Therefore, no significant polymerisation or other side reactions were found to interfere.

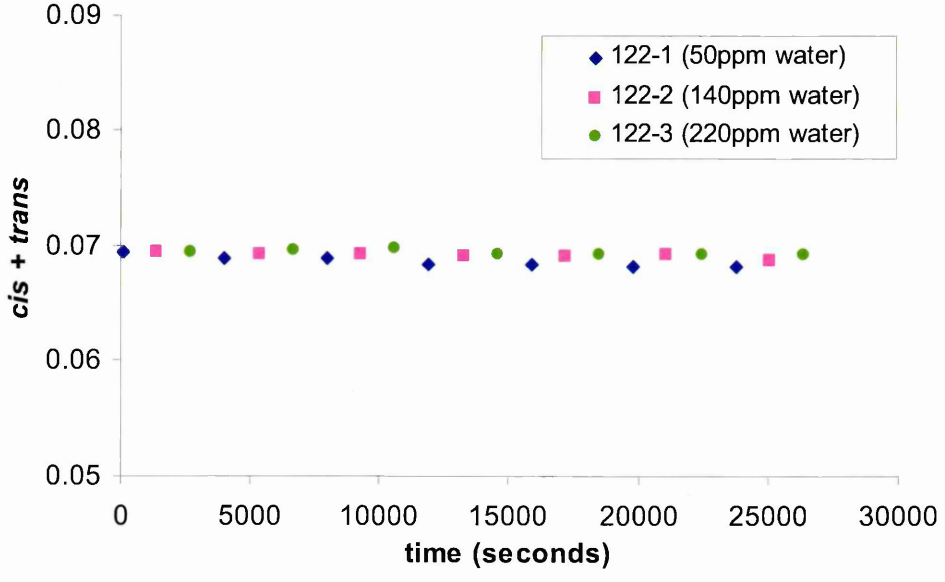


Figure 3.12 Interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.71 mM $FeCl_3$ at 60°C with various concentrations of water in nitromethane

It appears that a minimal amount of water is necessary for interconversion, possibly to generate a super acid. When excess water is present it coordinates with the proton to form a weaker acid, H_3O^+, and slows the reaction down. Similar inhibitory effects on interconversion are observed at even larger water concentrations; see Figure 3.13 (135-2, 135-3).

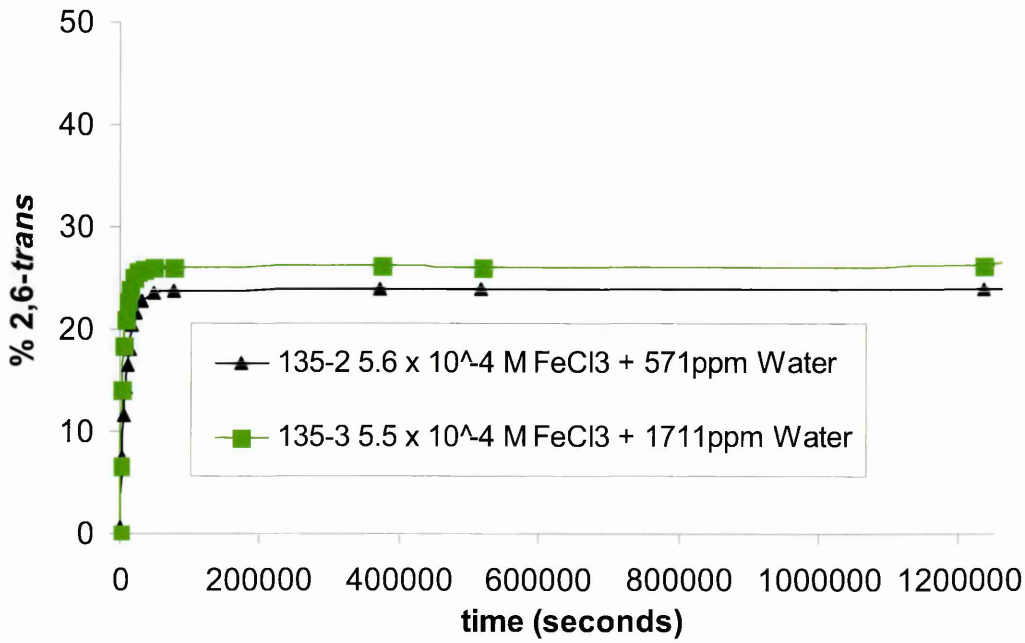


Figure 3.13 Interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by either iron chloride or aluminium triflate with various concentrations of water in nitromethane at 60°C

Figure 3.13 shows that the addition of 571 ppm water slowed the interconversion reaction and prevented it from achieving equilibrium. The sample with even more water (1711 ppm) inhibited the reaction as well. When too much water is present, it hydrolyses the super acid and eventually stops the interconversion reaction. The amount of water was found to have a large impact on the rate of polymerisation of cyclosiloxanes studied by other researchers.

Chojnowski et al. reported a 27 kJ mol^{-1} activation energy for the polymerisation of 1.5 M D_4 in CH_2Cl_2 catalysed with 0.3 mM triflic acid at 30°C.[64] The activation energy increased to 67 kJ mol^{-1} with the addition of 70 mM water. The rate of polymerisation increased as water was added, reaching a maximum, and then started to decrease as more water was added. The addition of water resulted in a drastically larger impact on the rate of D_3 polymerisation (10^{-2}) than on D_4 polymerisation (10^{-6}). (For comparison, the

interconversion of 19 mM 2,6-*cis* catalysed by 1.5 mM trifluoromethanesulphonic acid in nitromethane solvent at 30°C resulted in a rate constant of 1.46 x 10^{-4} s^{-1}).

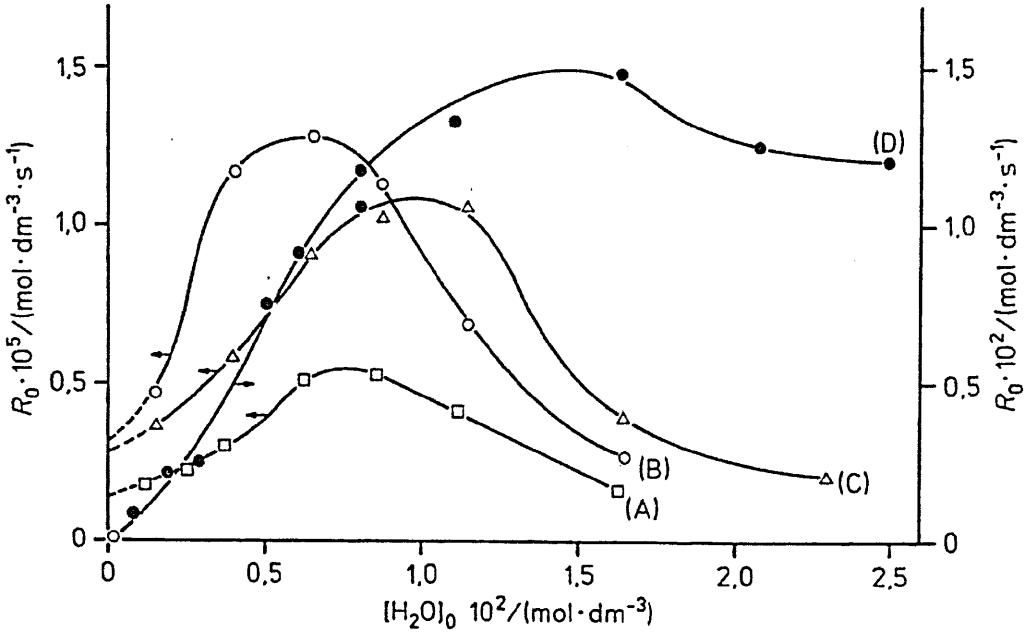


Figure 3.14 Effect of water addition on the initial rate of polymerisation of octamethylcyclotetrasiloxane (D_4) and hexamethylcyclosiloxane (D_3) in CH_2Cl_2 in the presence of CF_3SO_3H at 30°C. (A): $[D_4]_0$= 1.5 M, $[CF_3SO_3H]_0$= 2.5 x 10^{-4} M; (B): $[D_4]_0$= 1.5 M, $[CF_3SO_3H]_0$= 7.0 x 10^{-4} M; (C): $[D_4]_0$= 0.5 M, $[CF_3SO_3H]_0$= 7.0 x 10^{-4} M; (D): $[D_3]_0$= 2.0 M, $[CF_3SO_3H]_0$= 2.5 x 10^{-4} M

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In the complete absence of water (extrapolate the water concentration to 0 M in Figure 3.14 (D)), no appreciable reaction is predicted with D_3, and possibly D_4.

HA + SiOSi → SiA + HOSi (1) acidolysis

The complete exclusion of water is impossible for polymerisation due to the production of water from acidolysis/condensation (1), discussed in 1.3.3. Chojnowski et al. determined that the polymerisation was first-order in D_4 and second-order in acid. The order in acid decreased from 2.0 to 1.3 as water was added. The authors suggested that the order with

respect to acid would systematically reduce toward first order as larger amounts of water are added.

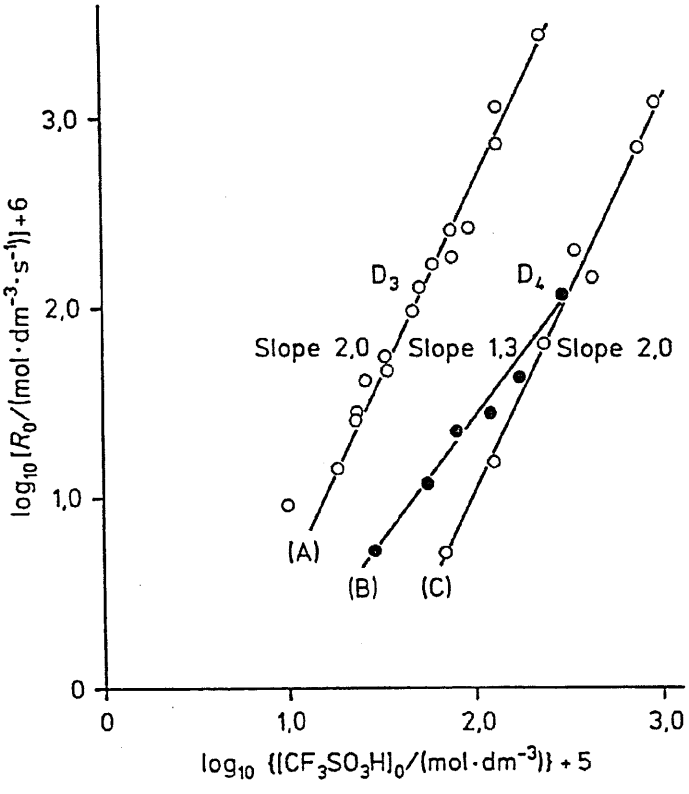

Figure 3.15 Dependence of the initial rage of polymerisation of hexamethylcyclosiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) in CH_2Cl_2 at 30°C, on the concentration of CF_3SO_3H. (A) and (C) (O): experiments with no additional water for D_3 and D_4, respectively; (B) (●); experiments with $[H_2O_2]_0$= 7 x 10^{-3} M for the polymerisation of D_4. Initial monomer concentrations: $[D_3]_0$= 2.0 M; $[D_4]_0$= 1.5M

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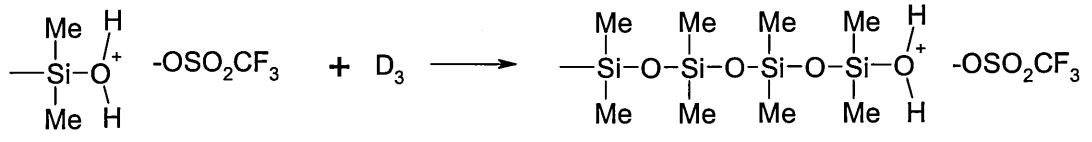
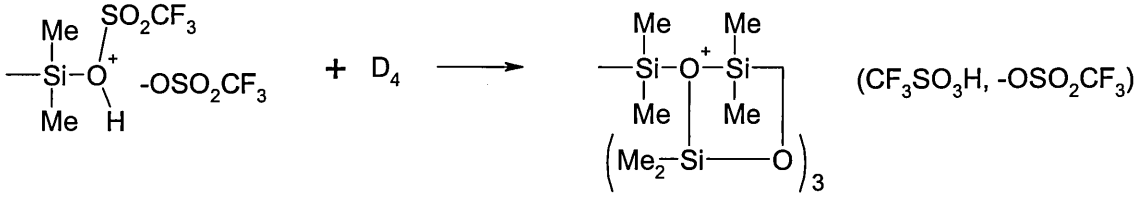
Chojnowski et al. reported similar results with D_3. A negative activation energy (-25 kJ mol^{-1}) was obtained for the polymerisation of 2.0 M D_3 catalysed by 8.0 x 10^{-4} M triflic acid at 30°C.[67] A positive activation energy (50 kJ mol^{-1}) was obtained for the polymerisation of 2.0 M D_3 catalysed by 2.1 x 10^{-4} M triflic acid when 3.0 x 10^{-2} M water was added at 30°C. Chojnowksi provides a partial explanation for the negative activation energy as being due to the destruction of active centres as the temperature increases.

Chojnowski et al. assume that condensation has a lower energy barrier than the cleavage of the siloxane bond; the siloxane bond cleavage is accelerated by a rise in temperature. This is not completely understood, and the negative activation energy is not observed with any other cationic polymerisation of cyclosiloxanes.

The polymerisation thus far has focused on acidolysis and provides a glimpse into the complexity of this cationic system. Overall, Chojnowski et al. and Sigwalt et al. offer similar mechanisms for polymerisation, where the difference resides in the type of oxonium ion propagating centre each proposes.

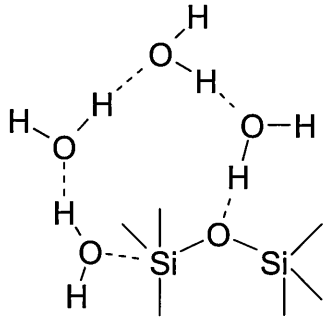




Many questions remain unanswered regarding the propagating species in cyclosiloxane polymerisation. The exact type of the proposed oxonium species is unknown because they have yet to be isolated, and it is unknown if they are transient or have a measurable lifetime.[129]

Cypryk and Apeloig performed ab initio calculations for the hydrolysis of disiloxane ($H_3SiOSiH_3$) that resulted in 34 kcal/mol for one hydrogen-bonded water molecule, and 22 kcal/mol for four hydrogen-bonded water molecules.[130] This shows that additional water molecules lower the energy barrier to hydrolysis. Protonation by a protic acid lowers the activation energy for hydrolysis to a larger extent. Attack of one water molecule on the protonated disiloxane was calculated at 26 kcal/mol, where the complex

containing four water molecules reduced the energy to 8.5 kcal/mol. Hydrogen bonded water clusters were proposed to reduce the activation barrier of hydrolysis of a protonated siloxane drastically through cooperative proton transfer from the nucleophile to the leaving group.



Protonation followed by nucleophilic attack of a hydrogen-bonded complex on silicon that allows access to the silicon backside is the lowest energy path to hydrolysis. The study with four hydrogen-bonded water molecules complexed with a silanol showed that the ability of the water cluster to hydrogen bond with the leaving group lowers the activation barrier to bond cleavage. Water will exchange a hydroxyl group with a silanol to produce water and silanol at essentially barrierless (1 kcal/mol) activation energies.

The amount of water changes the rate of the polymerisation reaction at low concentrations of acid (e.g. triflic acid). The H-bonding ability of water provides a possible path for the differences observed. Water can form an insoluble complex with triflic acid known as hydronium triflate (H_3O^+ $^-$Otf). The catalyst can exist as dimers or trimers which are postulated to vary in the presence of water. Water can form a complex with the acid that is in competition with the acid-acid interactions. At low catalyst concentrations, a large amount of these dimers and trimers seems unlikely. Small amounts of water may disrupt a cyclosiloxane-acid complex, while large amounts of water may cause a more active hydrated acid. These complications make it difficult to explain exactly the role of water in acid catalysed cyclosiloxanes polymerisation, and its impact on

the nucleophilicity of the conjugate base as well as its mobility and solubility.

Similar hydrogen-bonded complexes are expected to be present in the interconversion reactions. The order in acid approached first order for interconversion, but this included an excess amount of water (3.1 mM), which was present in the solvent. Additional amounts of water decreased the rate of interconversion and no polymerisation or other side reactions were found to interfere. The addition of water did not induce hydrolysis (3) in the interconversion studies, as has been observed under polymerisation.

More catalyst was post-added to the water inhibited interconversion reactions catalysed by iron chloride in Figure 3.13. This was performed in order to determine if the iron chloride catalysed interconversion was irreversibly inhibited by the excess water or if the extra catalyst could continue the interconversion. This also provides an indication that the rate of interconversion is faster than the rate of catalyst "deactivation" by water. After a period of time where the reaction slowed considerably, an additional 0.22 mM iron chloride catalyst was introduced to the two samples containing the extra inhibitory water (135-2 and 135-3). The interconversion was immediately restored (Figure 3.16).

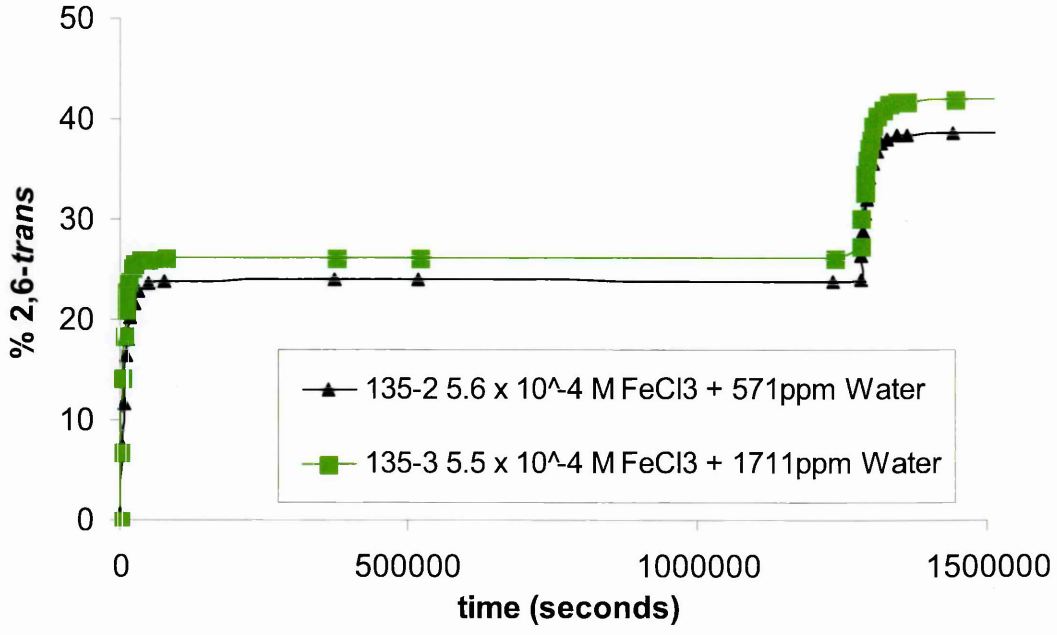


Figure 3.16 Interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by either iron chloride or aluminium triflate in nitromethane at 60°C, where the samples containing 571 and 1711 ppm water received 0.22 mM additional iron chloride

The interconversion reactions (samples 135-2, and 135-3) appear to fall short of the approximate 1:1 *cis*:*trans* equilibrium. The additional catalyst was either consumed or rendered inactive, presumably by the excess water in the system. The observed resumption of interconversion suggests that consumption of the catalyst occurred at a slower rate than the interconversion under these conditions. This is exemplified in experiment 135-2 of Figure 3.16, where once the additional catalyst was added the interconversion continued but did not reach the expected approximate 50:50 equilibrium mixture of the 2,6-isomers. This indicates the excess catalyst was bound, but not before some interconversion was catalysed by active catalyst.

Rodriguez and Moreno showed that an optical spectrum of a solution of 10^{-2} M iron chloride in *iso*-propanol containing 0.4M water produced 55% (±5%) $[FeCl_4]^-$; 20% $[FeCl_2(H_2O)_4]^+$, and the remaining 25% as dihydroxo dimers.[131] The same 55% result was

observed with a more concentrated 0.2 M iron chloride solution. Upon adding hydrogen chloride to the solution, the $[FeCl_4]^-$ peak increased, and all the iron (III) is eventually converted to $[FeCl_4]^-$, as long as enough Cl^- was provided. When the water was reduced to 0.02 M approximately 25% $[FeCl_4]^-$ was observed. As the concentration of water was systematically increased from 0.4 to 10 M, the $[FeCl_4]^-$ was progressively destroyed. The activity of the acid catalyst, pH, was reduced as water was added and other, *less catalytic*, complexes (such as $[FeCl_2(H_2O)_4]^+$, and dihydroxo dimers) formed. This is consistent with the reduction in iron chloride catalysed interconversion observed with inhibitory water.

Water is present in all the solvents used for interconversion, so in each case the catalyst may be hydrogen bonded or reacted with water. The nitromethane solvent contained approximately 50 ± 5 ppm of water. The role of water is important because it has also been reported that dry Lewis acids do not catalyse the polymerisation of cyclosiloxanes (Section 1.3.3).[69] The addition of water slows the rate of interconversion of 2,6-*cis* catalysed by 0.71 mM iron chloride in nitromethane. The large molar excess addition of 8.8 mM and 13.8 mM water reduced the interconversion rate, but did not prevent the reaction. Addition of greater than 13.8 mM water also prevented the interconversion from achieving completion. No polymerisation products were observed in these reactions.

Protonation reduces the energy barriers of the siloxane bond cleavage. Cypryk and Apeloig's calculations support Wilczek and Chojnowski's proposal of water trimers and tetramers as the active species necessary for proton transfer in acid-catalysed siloxane bond cleavage.[60] A pentacoordinate silicon transition state complex was supported along with H-bonded clusters where the local concentrations of reagents were very high. Cypryk and Apeloig suggest the real rate constants may be very different from those

obtained using classical kinetic laws, which are based upon total concentrations of reactive species in solution.[130]

3.4.1 Proton Sponge

A proton sponge can be used to bind protons, as was attempted in Chapter 2. Removal of protons with the addition of a proton sponge (1.5 molar excess of proton sponge (tetramethyl-1,8-naphthalenediamine) or 2,6-di-*tert*-butyl-4-methylpyridine (DBMP)) to the catalyst solution resulted in no interconversion or polymerisation of 2,6-*cis* catalysed by iron chloride over several days. The amine/pyridine proton sponges did not supply additional water to the reaction, based on the Karl Fischer titration results. The rate of 2,6-*cis* interconversion was reduced (Figure 3.17) when the proton sponge was added initially with the aluminium triflate catalyst prior to heating.

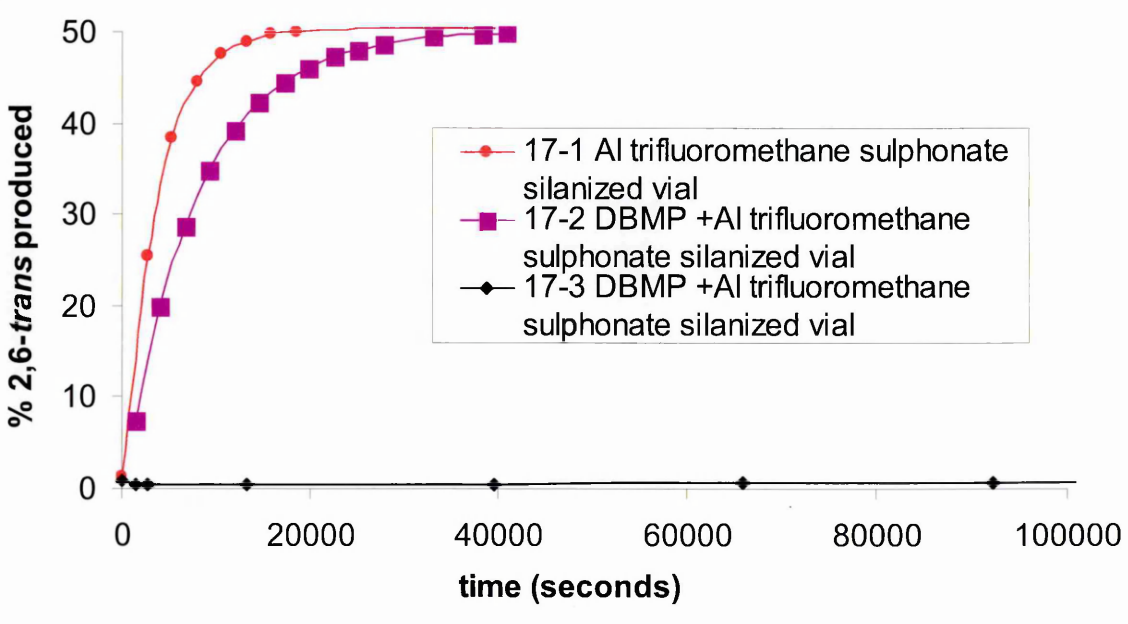


Figure 3.17 Interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by aluminium triflate in nitromethane at 40°C with various concentrations of the proton sponge DBMP (2,6-di-*tert*-butyl-4-methylpyridine)

A control sample (17-1) contained 21 mM 2,6-*cis* and 1.6 mM aluminium triflate

in nitromethane with no proton sponge. This sample rapidly interconverted the substrate to the equilibrium *cis*:*trans* mixture at 40°C, where the first-order rate constant was measured as 2.48 x 10^{-4} sec^{-1}, see Appendix C for data. A similar interconversion sample (17-2 containing 21 mM 2,6-*cis* and 1.6 mM aluminium triflate in nitromethane) which contained a sub-stoichiometric amount of proton sponge, 0.69 mM DBMP, achieved completion, although at a slower rate, 1.28 x 10^{-4} sec^{-1}, than 17-1. A sample (17-3) containing an excess of proton sponge and a similar concentration of catalyst (1.6 mM aluminium triflate) did not interconvert the 21 mM 2,6-*cis* because more proton sponge (2.1 mM DBMP) than catalyst was added. This sample resulted in no reaction observed over the time period studied. The inhibition of 1.6 mM aluminium triflate with 2.1 mM DBMP may indicate an aluminium triflate-DBMP complex. Three mole of triflic acid could be produced for every mole of aluminium triflate, unless the basic impurity is present in sufficient amount. The interconversion of 20 mM 2,6-*cis* catalysed by 18.9 mM triflic acid (14-1) produced a rate constant of 2.6 x 10^{-5} sec^{-1} at 40°C. The interconversion of 21 mM 2,6-*cis* catalysed by approximately ten times less catalyst (1.6 mM aluminium triflate (17-1)) is ten times faster, with a 2.48 x 10^{-4} sec^{-1} rate constant. This shows that interconversion catalysed by aluminium triflate is much faster than the three times faster than triflic acid, assuming the three triflate anions in aluminium triflate hydrolysed fully to produce three triflic acid molecules.

If less proton sponge was added, the interconversion achieved equilibrium (Figure 3.18), but the rate of the reaction was reduced relative to proton trap.

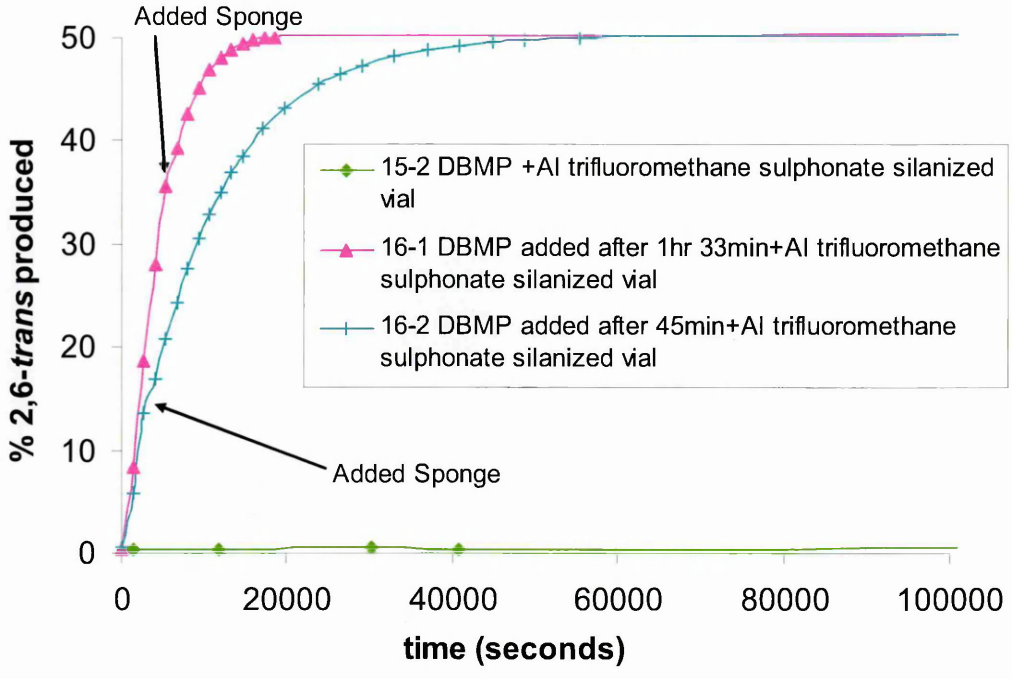


Figure 3.18 Interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by aluminium triflate in nitromethane at 40°C with various concentrations of the proton sponge DBMP (2,6-di-*tert*-butyl-4-methylpyridine) added at different times

A sample (16-1) containing 20 mM 2,6-*cis* and 1.6 mM aluminium triflate catalyst in nitromethane solvent (Figure 3.18) was allowed to react at 40°C. After 1 h 33 min a proton sponge, 0.16 mM DBMP, was added with minimal impact upon the extent of ultimate conversion to the isomeric mixture, but a reduction in rate of conversion was observed. A similar sample (16-2, containing 20 mM 2,6-*cis*, catalysed by 1.6 mM aluminium triflate) was allowed to interconvert for 45 minutes before a larger concentration of proton sponge (0.23 mM DBMP) was added. The rate of interconversion was reduced even further with the addition of this larger concentration of proton sponge, but the interconversion products were the same. Excess proton sponge (1.4 mM DBMP) was added to sample 15-2, which contained 21 mM 2,6-*cis* catalysed by 0.83 mM aluminium triflate, which prevented the interconversion reaction.

The addition of the proton sponge reduced the rate of the interconversion catalysed

by aluminium triflate or prevented the reaction depending on the concentration of proton sponge used. No polymerisation was observed either. The Lewis acid catalysed interconversion reaction was prevented when the proton was bound by a sponge, unless the proton sponge had reacted with the Lewis acid.

Kendrick showed that neither anhydrous ferric chloride nor anhydrous HCl catalyse the polymerisation of D_4 (octamethylcyclotetrasiloxane).[69] Brown and Kanner first reported the use of hindered pyridines to differentiate between protic and Lewis acids.[71] They showed no complexation of BF_3 with 2,6-di-*tert*-butylpyridine. Gandini et al. reported that the addition of the proton sponge DBMP did not affect the rate of aluminium triflate catalysed polymerisation of isobutene.[73] They used ^1H nuclear magnetic resonance (NMR spectroscopy) to show an interaction between the Lewis acid and water, and more importantly, a lack of interaction between the free Lewis acid and DBMP or $HDBMP^+$.[73] Jordan concluded from Gandini's work that Lewis acids do not react with proton sponges. Jordan observed no reaction of 0.9 M D_3 with 2.3×10^{-4} M EBST (ethylboron sesquitriflate) when 2.5×10^{-4} M DBMP was added in a 76/24 volume mixture of CH_2Cl_2/CH_3CN, where no polymer was formed even after 10 days at 25°C.[70] Without a proton sponge, 1.7 M D_3 catalysed by 2.5×10^{-4} M EBST in a 84/16 volume mixture of CH_2Cl_2 /CH_3CN produced 63% polymer in 18 hours at 25°C. Addition of more EBST catalyst or water induced polymerisation. Gandini addresses Sigwalt's 1983 claim of an aluminium chloride DBMP complex only as "peculiar" and deserving "further attention". The literature above suggests no complexation between a Lewis acid and a proton sponge, but the following references suggest otherwise. Sigwalt et al. reported a calculated nitrogen-to-aluminium bond distance $\cong$ 2Å in an $AlCl_3$-DBMP distorted tetrahedron model.[76] The authors compare this distance to the 1.847 Å observed by X-ray for the aluminium-to-oxygen distance in the complex between CH_3CH_2COCl and $AlCl_3$.

Interestingly, no interaction was observed in the ^{1}H NMR spectrum for a DBMP-$TiCl_4$ complex. The authors attempt to explain the absence of complexation in terms of the bulkier and symmetrical tetrahedron around the Ti than Al and a weaker acidity, but conclude with the comment "the effects of sterically hindered pyridines in cationic polymerisation are not as simple as indicated by previous investigators".[76] In 1996, Bennevault et al. showed that sterically hindered amines (DBMP and DBP(2,6-di-*tert*-butylpyridine)) inhibit the polymerisation of chloroethyl vinyl ethers with $ZnCl_2$.[75] Bennevault et al. modelled the $ZnCl_2$-DBP complex, which resulted in a 1.94 Å distance between the nitrogen and zinc atoms.[75]

The above examples show that a proton sponge can inhibit or completely prevent the Lewis acid catalysed interconversion reaction. Enough prior art exists for a proton sponge-Lewis acid complex that an iron chloride-DBMP complex and possibly an aluminium triflate-DBMP must be considered as the reason catalysis of interconversion is prevented. Thus, the above proton sponge experiments cannot support the removal of just the proton, and the role of the proton in the Lewis acid catalysed interconversion is not completely understood. The use of a proton sponge is an ineffective method to distinguish protons in our system. Protons may be necessary for both interconversion and polymerisation reactions, as evident when the addition of a proton sponge prevented both reactions, although an acid-proton sponge complex can not be dismissed.

More evidence for a proton sponge- Lewis acid complex was obtained from a set of ^{1}H NMR experiments. The chemical shift in the ^{1}H NMR spectrum associated with a proton trapped by a proton sponge was determined first. All experiments were carried out in deutrated nitromethane. Triflic acid, (B) in Figure 3.19, is shown to have a peak at approximately 12.5 ppm, representing the proton on this acid.

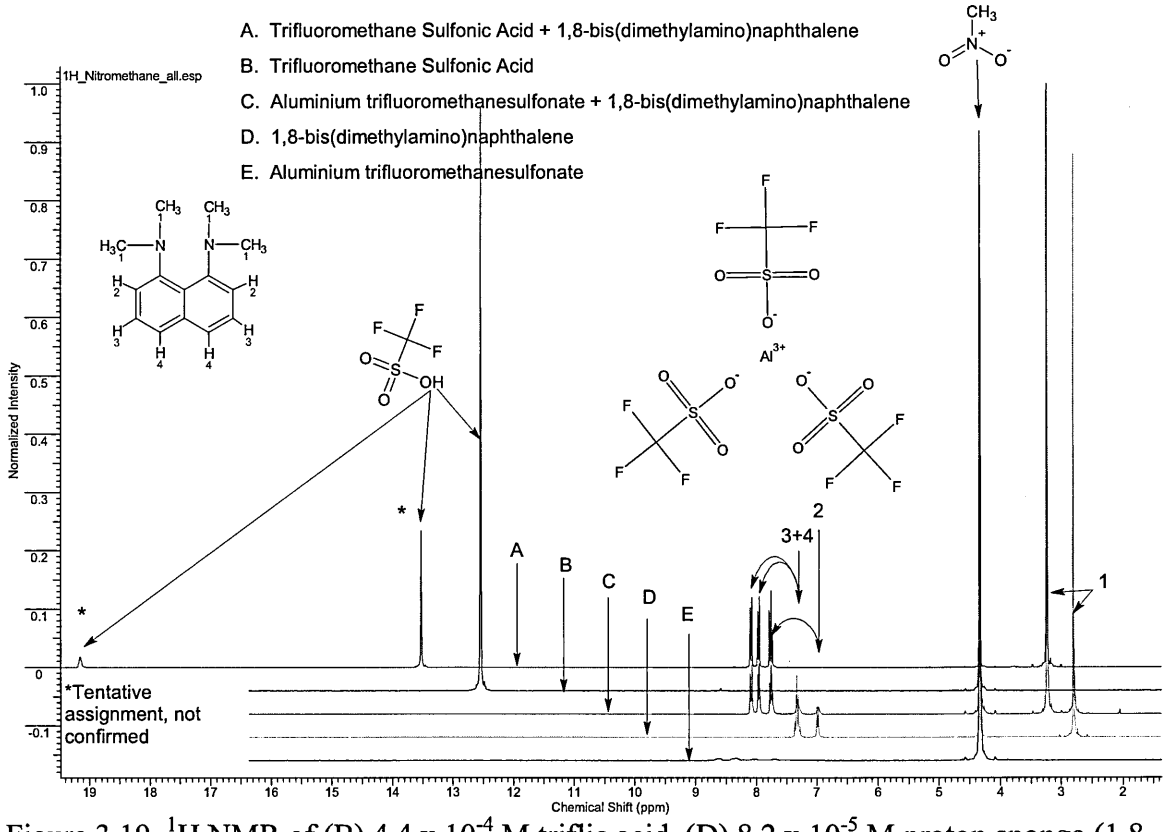


Figure 3.19 ^{1}H NMR of (B) 4.4 x 10^{-4} M triflic acid, (D) 8.2 x 10^{-5} M proton sponge (1,8-bis(dimethylamino)naphthalene), (A) 4.4 x 10^{-4} M triflic acid + 1.2 x 10^{-4} M proton sponge, (E) 7.3 x 10^{-5} M aluminium triflate, and (C) 9.3 x 10^{-6} M aluminium triflate + 3.9 x 10^{-5} M proton sponge, all in nitromethane-d_3

When triflic acid is combined with a sub-stochiometric amount of proton sponge (1,8-bis(dimethylamino)naphthalene) the proton shifts from 12.5 to 13.5 ppm or possibly 19 ppm (spectrum (A)), and the aromatic protons shift approximately from 7 to 8 ppm. This indicates the proton is possibly trapped by the proton sponge at 19 ppm. No protons are observed in the aluminium triflate sample (spectrum (E)) suggesting no free acid or water. When the proton sponge is combined with aluminium triflate (spectrum (C)) the aromatic protons are shifted from approximately 7 ppm to 8 ppm, and the dimethyl protons are shifted from 3 ppm to approximately 3.5 ppm, and there is evidence of proton sponge starting material. These data suggest an aluminium triflate-proton sponge complex is probably present as no acidic H^{+}'s are present in (C), and complexed as well as non-

complexed aromatic peaks are present. An averaged peak may be expected if a proton was complexed with the proton sponge, as fast exchange would be expected.

3.5 Effect of Solvent

Frye and Spielvogel showed that the interconversion between 2,6-*cis* and 2,6-*trans* was effective only with polar aprotic solvents.[80] Nitroalkanes were their primary examples of solvents used for this interconversion. Thus, a majority of our research involved nitromethane as the solvent. The solvent provides a polar medium for the interconversion reaction. It could also provide a nucleophile for the transition state mechanism of interconversion. The oxygen from the nitroalkane could act as a nucleophile and donate its electrons to the silicon to form a pentacoordinate intermediate. This intermediate could then pseudorotate several times to form the other stereoisomer. No interconversion was observed without a catalyst under the attempted conditions within the time scale studied. This does not rule out the role of a solvent since the interconversion only takes place with a very specific type of solvent, namely polar aprotic solvents. Changing from aprotic to protic solvent affects the acidity or basicity, since there is a difference in solvation of anions by a protic solvent which can form hydrogen bonds.[93]

In an attempt to test the hypothesis that protic solvents are ineffective for interconversion, the protic solvent 1-butanol was evaluated as the solvent for the interconversion with iron chloride as the catalyst. A solution containing 6.2 mM iron chloride, 10 mM 2,6-*cis*, and 12 mM naphthalene in 1-butanol was analysed by the same GC method as used above at 60°C. Within a short period of time 2,6-*trans* was observed along with other peaks that eluted at longer retention times, indicative of rearrangement/polymerisation. These other peaks were most likely larger cyclics and/or

linears that were formed. Interconversion of 2,6-*cis* was observed with a polar aprotic solvent, while other cyclics and linears were formed when the solvent was polar protic such as 1-butanol. In this case, 1-butanol may be acting as a nucleophile (or forming a stronger nucleophile with the acid than the acid alone) toward silicon, cleaving the Si-O bond and inducing the polymerisation. The butanol could also be hydrolysing the catalyst. Polar protic solvents are ineffective media for interconversion without polymerisation.

A study of polar aprotic solvents was undertaken in order to further understand the role of the solvent. The interconversion of 2,6-*cis* was followed by GC when catalysed by iron chloride in the various solvents listed in Table 3.9.

Solvent	2,6-*cis* cyclic (mM)	$FeCl_3$ catalyst (mM)	% 2,6-*trans* w/ 1x catalyst	% 2,6-*trans* w/ 2x catalyst	Water ppm (Karl Fischer)
acetonitrile (CH_3CN)	8.3	0.72	50% (<1.5 hrs)	NA	80
nitromethane	20.5	0.51	50% (2.5 hrs)	NA	50
2-nitropropane	18.8	0.57	50% (40%, 2hrs)	NA	155
nitrocyclohexane	7.4	0.69	<1% (1 day)	50% (2 months)	
1-nitrobutane	8.8	0.58	<5% (4%, 1 day)	<5%	249
DMSO (C_2H_6SO)	7.6	0.49	<5% (2%, 14days)	NA	190
nitrocyclopentane	9.2	0.42	5% (2days) 1% (12 days)	20-25%	946
nitrobenzene	11.0	0.94	50% (2 months)	NA	28
0.0034g $FeCl_3$ in 2ml CH_3NO_2		10.48			132

Table 3.9 Interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by iron chloride in various polar aprotic solvents at 60°C

Interconversion occurred at a rapid pace with acetonitrile, nitromethane, and 2-nitropropane. Interconversion was quite slow when run in the larger analogues. The water content in the solvents as supplied, measured by Karl Fischer titration, does not appear to correlate with the rate of interconversion. Water is present in all these solvents, so in each case the iron chloride may be altered from its pure form, reacting with the water and reducing the acid strength. The polarity of the medium decreases as the R-group on the nitroalkane increases, causing the ionic transition state to be less stabilised. There is

relatively less NO_2 to act as the nucleophile as the size of R-group increases. The interconversion reaction rate is faster in acetonitrile, which may indicate that it is relatively more nucleophilic.

Polar aprotic solvents, namely nitroalkanes and acetonitrile, were necessary in all of the reactions studied in order to produce interconversion products. The solvent provides a polar medium favourable for the interconversion reaction. It could also provide a nucleophile that can attack the silicon to form a pentacoordinate moiety which acts as the transition state or intermediate in the mechanism of interconversion.

When a protic solvent was used, e.g. 1-butanol, the products reflected typical ring-opening polymerisation of cyclosiloxanes even at low catalyst concentrations. No reaction was observed with the nonpolar solvent pentane. Polar protic solvents induced polymerisation, and only polar aprotic solvents were shown to support interconversion. Polar solvents are capable of supporting ionic species. This may indicate that charged species are formed during interconversion. This is not the case for a nonpolar medium.

The interconversion of dilute solutions of cyclosiloxanes in solvent surely will favour intramolecular reactions.

3.6 Other Cyclosiloxanes

The interconversion reaction of cyclosiloxanes other than 2,6-*cis* and 2,6-*trans* was part of the original objective. Pure isomers of all cyclosiloxanes are not readily available. The separation of isomers from several cyclosiloxane mixtures was attempted in our laboratory.

Numerous attempts to separate the stereoisomers of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisiloxane were unsuccessful. Vacuum distillation typically resulted in a polymeric mixture in the flask. The use of a rearrangement catalyst (e.g. LiOH) with

either a cyclic or a linear starting material did not improve the production or separation of the cyclic isomers. Crystallisation of the cyclic trimer was attempted from both methanol and pentane. No crystals were observed after several months of refrigeration. Similar attempts to separate the isomers of 2,4,6-trimethyl-2,4,6-trivinylcyclotrisiloxane were also unsuccessful.

The *cis* and *trans* isomers of 2,4,6-*tris*trifluoropropyl-2,4,6-trimethylcyclotrisiloxane can be easily separated by crystallisation. At room temperature the pure *trans* isomer is a solid, while the pure *cis* isomer is a liquid. Thus, the isomers can be separated from a solventless mixture by slightly warming the solution and allowing the material to crystallise. The samples used in this study were heated to 40°C and cooled in a freezer to speed the crystallisation process. The samples were then filtered and the process repeated to produce >95% *trans* isomer. The *cis* isomer was further purified by recrystallisation from 1-butanol. The purity was assessed by GC. Materials that eluted later than the starting material were observed and presumed to be larger cyclics and linears. The initial conditions for the flame ionisation GC were 310°C for the injector and 300°C for the detector. It was presumed that the high temperatures used for the GC may have caused rearrangement. In another analysis, the injector and detector temperatures were decreased to 200°C. The materials eluting after the D_3 were still present, so reducing the temperature did not solve this rearrangement issue. Solvent was used to dilute the cyclic samples in order to avoid swamping the detector with sample. The initial choice of solvent was acetone. This turned out to be a poor choice, as the acetone appears to rearrange the trifluoropropyl cyclics at the elevated temperatures of the injector. Only the two desired isomers were observed in the GC after the solvent was switched to n-heptane. This supports the proposal that acetone as the solvent was responsible for the production of larger cyclics/linear siloxanes. The interconversion reaction with these isomers was not

attempted, but would be a natural extension of this work.

3.7 Summary

Interconversion of 2,6-*cis* or 2,6-*trans* was shown to occur with Lewis acids in a manner similar to the results obtained in Chapter 2 with Brönsted acids. The relative rates of two competing reactions, interconversion and polymerisation, can be adjusted on the basis of catalyst choice as well as its concentration and reaction temperature. A similar analytical method was used to determine that the interconversion 2,6-*cis* is first-order in both the Lewis acid catalyst and the cyclosiloxane starting material. The reaction can be described as $J = k\,[2,6\text{-}cis]^1[FeCl_3]^1$ becoming second-order overall. First-order in iron chloride catalyst was obtained with a corrected acid concentration. A portion of the acid may have been consumed by a base, which may be present as an impurity in the nitromethane solvent. The presence of other impurities, including moisture, was shown to change the nature of the nucleophile. Similar results were obtained for the interconversion reaction catalysed by triflic acid in Chapter 2. The addition of water inhibited the interconversion reaction catalysed by a Lewis acid in a polar aprotic solvent.

The addition of a proton sponge prevented both interconversion and polymerisation reactions. Pure Lewis acids do not catalyse polymerisation, as protons are necessary. A complex of the Lewis acid and proton sponge could not be dismissed. Thus, the presence of protons is hypothesised as necessary for both reactions, but cannot be fully supported with the proton sponge experiments due to the possible formation of a proton sponge-Lewis acid complex.

The activation energy for the interconversion of 2,6-*cis* isomer catalysed by 0.43 and 0.18 mM (corrected) iron chloride was determined to be 55.2 and 66.1 kJ mol^{-1}, respectively. The entropy of activation $\Delta S^{\ddagger}$ for interconversion for these conditions was

determined to be -149 and -123 J/mol K and the enthalpy of activation $\Delta H^{\ddagger}$ is 52.5 and 63.4 kJ/mol respectively. The entropy of activation $\Delta S^{\ddagger}$ for the interconversion catalysed by triclic acid was determined to be -186 J/mol K and the enthalpy of activation $\Delta H^{\ddagger}$ was 21.8 kJ/mol.

Polar protic solvents induced polymerisation, and only polar aprotic solvents were shown to support interconversion. No reaction was observed with the nonpolar solvent pentane.

The interconversion reaction was determined to be first order in catalyst and siloxane, where a stable pentacoordinate silicon intermediate is proposed. Pseudorotation of this pentacoordinate intermediate is the proposed pathway for interconversion of the stereoisomers. The results of interconversion catalysed by iron chloride are very similar to the triflic acid results, and the proposed mechanisms are similar. The difference is the nature of the species coordinated to the oxygen—either a proton or a Lewis acid complex.

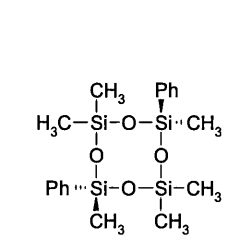
Chapter Four

Discussion & Conclusions

4 Discussion

4.1 Conclusions

A reaction mechanism is a sequence of elementary steps that define the path between reactants and products. Analytical determination of an intermediate provides supporting evidence for a reaction pathway, but these highly reactive species can be short-lived. This appears to be the case with the interconversion reaction studied. An indirect method was used to probe the mechanism of interconversion. A GC method was developed to follow the progression of reactions. The interconversion from 2,6-*cis* to an equimolar (49.8% 2,6-*cis* : 50.2% 2,6-*trans*) mixture was determined to obey first-order kinetics with respect to the starting material and the catalyst (after accounting for the inactive catalyst) for triflic acid and iron chloride, while second order in methanesulphonic acid was determined. A summary of the findings of the acid-catalysed reactions of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane is displayed in Figure 4.1.



2,6-*cis* diphenylhexamethyl-cyclotetrasiloxane

Lewis Acid ($FeCl_3$) → 50:50 mixture
Polar Aprotic Solvent (RNO_2) → 2,6-*cis/trans isomers*

+Proton Sponge
or hindered pyridine → No Rxn

in Polar Protic Solvent → oligomeric and cyclic distribution

Common Bronsted Acid "nucleophilic" counterion → oligomeric and cyclic distribution
Polar Aprotic Solvent

Bronsted Acid "weakly-nucleophilic" counterion → 50:50 mixture
Polar Aprotic Solvent → Interconversion

Polymerisation is observed with high concentrations of catalyst or long periods of heating.

Figure 4.1 Conditions for interconversion versus polymerisation of 2,6-diphenylhexamethylcyclotetrasiloxane

The first step in both reactions appears to be protonation or metal complexation with an oxygen in the cyclosiloxane ring. Both interconversion and polymerisation involved a negative activation entropy, which supports a more ordered transition state, such as a pentacoordinate silicon. The second mechanistic step appears to be nucleophilic attack forming a pentacoordinate silicon intermediate. In polymerisation, the siloxane bond is broken, forming a tetracoordinate silicon. The activation energy for polymerisation was shown to be two to three times that for interconversion when catalysed by methanesulphonic acid. A proposed mechanism for interconversion is a series of pseudorotations of the pentacoordinate intermediate. The result is an interconversion of the starting material into the opposite stereoisomer once the nucleophile leaves. A reaction coordinate diagram representation of this is shown in Figure 4.2.

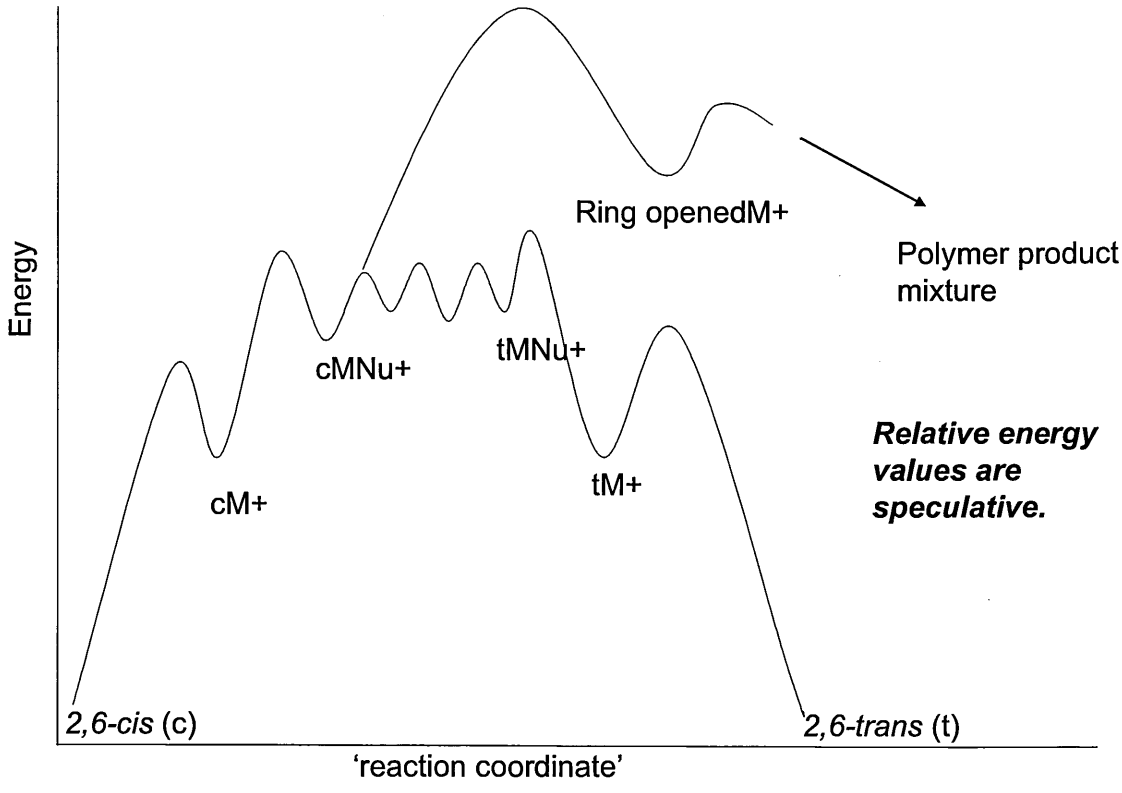


Figure 4.2 Energy diagram representation for cyclosiloxane pentacoordinate silicon intermediate formation followed by pseudorotation for interconversion to the *trans* isomer or ring opening to polymerisation products (M^+= metal complex, and may be substituted for H^+).

The relative rates of two competing reactions, interconversion and polymerisation, can be adjusted on the basis of catalyst choice as well as its concentration and reaction temperature.

Interconversion and polymerisation are competing reactions in this acid catalysed system which share mechanistic steps. The stability of the pentacoordinate silicon intermediate determines the balance between interconversion and polymerisation products. Interconversion of the systems studied can be represented as the probability of pseudorotation of the pentacoordinate silicon intermediate in Figure 4.3.

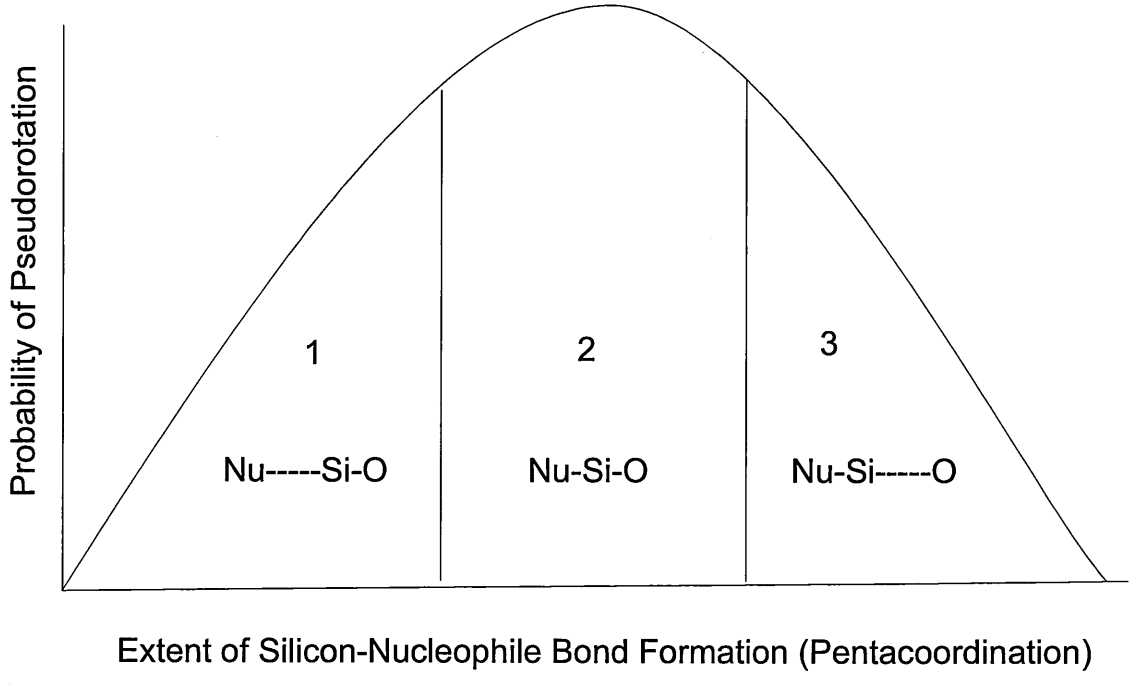


Figure 4.3 Representation of proposed pentacoordinate silicon intermediates for (1) no reaction; (2) interconversion; and (3) polymerisation.

Several factors can impact the stability of the pentacoordinate silicon intermediate, including protons, temperature, solvent, and nucleophiles as specifically studied in this thesis. The extent of pentacoordination is small with very poor nucleophiles and Si-O bond cleavage will be unlikely. Pseudorotation is also unlikely in this case as the energy barriers are too high and the Si-Nucleophile bond breaks to give back the starting materials before pseudorotation occurs, as represented in area 1 of Figure 4.3. No reaction was observed when 2,6-*cis* was dissolved in nitromethane. There is no protonation of the siloxane oxygen to improve the leaving group ability and the nitromethane is a poor silicon nucleophile in this system. Once the siloxane oxygen has been protonated to make it a good leaving group the intermediate nucleophiles (e.g. methane sulphonate) produce a reasonable amount of Si-Nucleophile bond formation, but not too much Si-O bond breaking in area 2 of Figure 4.3. In this case, pseudorotation has time to occur before Si-Nucleophile bond cleavage occurs to give back the starting materials. Over a longer time

period the nucleophile is strong enough to lead to ring opening and then polymerisation. Stronger nucleophiles (Cl^-, HSO_4^-) tend toward polymerisation. These good nucleophiles attack the silicon leading to substantial Si-O bond cleavage such that the pentacoordinate silicon intermediate has a short lifetime and little chance to pseudorotate before Si-O bond cleavage, as represented in area 3 of Figure 4.3. Chang et al. showed the interconversion of 1,3,5-*cis*-trimethyl-1,3,5-triphenylcyclotresiloxane to the expected equilibrium *cis* to *trans* isomeric mixture in DMSO catalysed by n-$C_8H_{17}NH_3BF_4$.[82] This weak acid ($RNMe_2$-H^+) acts as a hydrogen bonded complex with silicon ($RNMe_2$-H^+--O-Si), and is a poor leaving group. A stronger nucleophile is needed (possibly F^- or HF) to achieve pseudorotation but not strong enough to lead to Si-O bond cleavage, and ring opening. The diagram in Figure 4.4 is an illustration that details the extent of bonding for the silicon-nucleophile (Si-Nu) and the silicon-oxygen (Si-X).

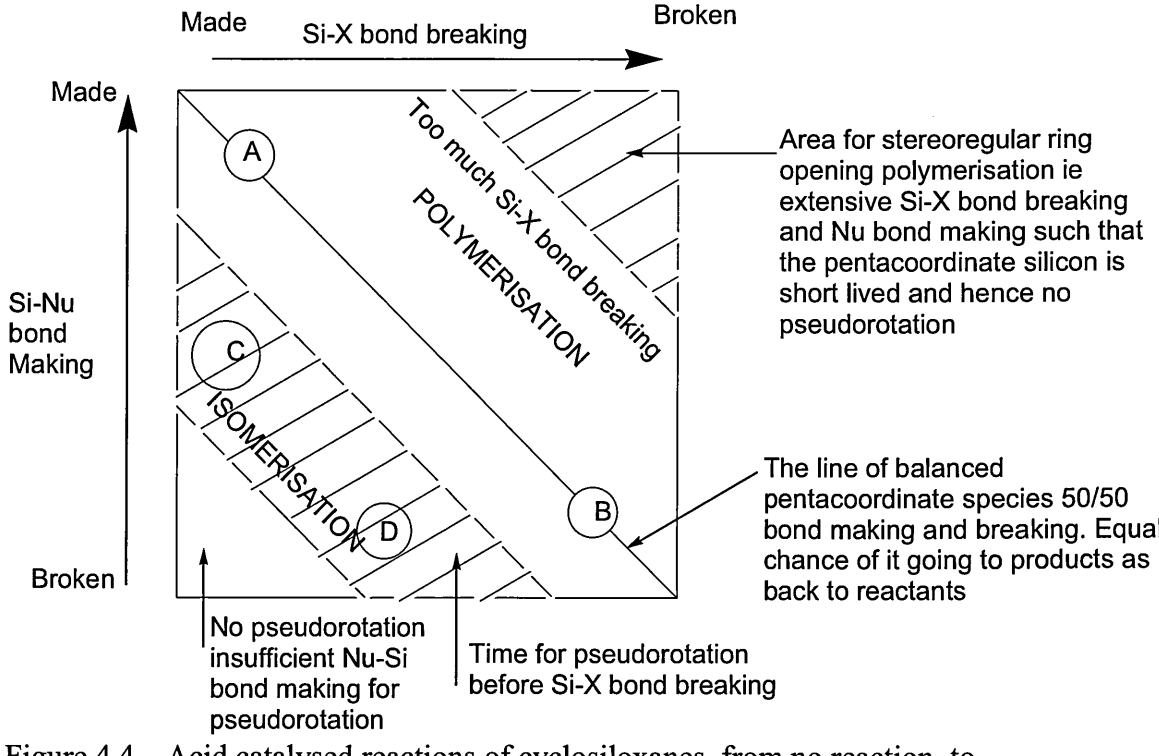
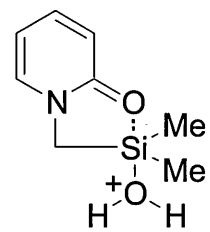


Figure 4.4 Acid catalysed reactions of cyclosiloxanes, from no reaction, to interconversion, to polymerisation

In Figure 4.4 point A is a tight pentacoordinate state such as in SiF_5^-, and point B represents more of a loose pentacoordinate state more like a complexed siliconium ion.



Point C could represent a pentacoordinate complex (e.g. that observed by Chang et. al.) with little Si-O bond breaking because the ammonium salt is a weak acid and more extensive Si-X bond making as the nucleophile is possibly F^-. Point D represents the pentacoordinate complex we have studied with methane sulphonic acid or triflic acid – little Nu-Si bond making.

4.2 Implications for Acid-catalysed Polymerisation of Cyclosiloxanes

Many researchers have reported complex orders (2.0 to 3.5) in catalyst for protic acid catalysed ring-opening polymerisation of cyclosiloxanes. The origin of these complex orders has not been fully detailed, but may involve a complex of the acid as dimers or trimers. Initial zero and negative orders in catalyst measured during the early stages of polymerisation have also been reported. Sigwalt observed an induction period with lower concentrations of catalyst.[66] No explanation that completely satisfies all of the observations has been provided. The initial changing rates of acid catalysed cyclosiloxane polymerisation may be the result of side reactions where the catalyst is involved and thus cannot participate in the polymerisation reaction. Similar results were observed in the interconversion reaction and its rate reduction observed upon the addition of water.

The interconversion reaction of 2,6-*cis* may indicate the difficulty in synthesis of stereoregular polymers from cyclosiloxanes. Acid-catalysed reactions of cyclosiloxanes have been observed, in some of the systems studied, to be a balance between interconversion and polymerisation. Interconversion will alter the stereospecific starting material into a mixture of isomers before and possibly during polymerisation. Figure 4.4 suggests that stereoregular polymerisation is unlikely with a weak nucleophile. This may lend some insight into the difficulties researchers have experienced with acid catalysis of cyclosiloxane conversion to form isotactic or syndiotactic polymers. Chain extension is faster than back-biting and chain transfer with anionic polymerisation of cyclotrisiloxane, which is why it is used for selective polymerisation to form isotactic or syndiotactic polymers.[132]

Chapter Five

Experimental

5 Experimental

5.1 Description and Sources of Materials

All materials and equipment were obtained from sources within the United States unless otherwise noted. 2,6-*cis*-Diphenylhexamethylcyclotetrasiloxane (2,6-*cis*), 2,6-*trans*-diphenylhexamethylcyclotetrasiloxane (2,6-*trans*), and 2,4,6-triphenyl-2,4,6-trimethylcyclotrisiloxane were obtained from Dow Corning Corporation (Midland, MI). The 2,6-*cis* was determined to be 99% pure by gas chromatography (GC). Nitromethane (Sigma-Aldrich, St. Louis, MO) was determined to be 99+% pure by GC-mass spectroscopy (GC-MS) and was stored over 3 Å molecular sieves (Sigma-Aldrich, St. Louis, MO) before use. A GC-MS of this solvent agreed with the molecular weight of CH_3NO_2. The acid catalysts, trifluoromethanesulphonic acid (triflic acid), methanesulphonic acid, iron chloride, zinc chloride, aluminium triflate, lanthanum triflate, and ytterbium (III) triflate were obtained from Sigma-Aldrich (St. Louis, MO) and were used as received. The proton sponges (tetramethyl-1,8-naphthalenediamine and 2,6-di-*tert*-butyl-4-methylpyridine) and the internal standard naphthalene (99+%) were obtained from Sigma-Aldrich (St. Louis, MO). The protic acids HCl, H_2SO_4, and HNO_3 were purchased from Fisher Scientific (Pittsburgh, PA). The solvents acetonitrile, nitrocyclohexane, 2-nitropropane, dimethylsulphoxide, nitrocyclopentane, 1-nitrobutane, and nitrobenzene were obtained from Sigma-Aldrich (St. Louis, MO). Ultra pure water was obtained from a Milli-Q system at the Dow Corning Corporation (Midland, MI).

5.2 Sample Preparation

Precautions were taken to exclude moisture when handling moisture-sensitive compounds, but the possibility of a small percentage of hydrolysis cannot be discounted.

Catalyst dilutions were performed in a glove box (Model HE-43-2, Vacuum Atmospheres, Hawthore, CA) with oven-dried volumetric flasks (Fisher Scientific, Pittsburgh, PA) and sealed in oven-dried, crimp-top GC vials (Agilent, Palo Alto, CA) before removing from the glove box. The glove box was purged with 99.995% argon (Michigan Air Gas, Midland, MI), which was dried through the Dri-train which contained two molecular sieve/copper catalyst drying/regeneration beds (Dri-train Model MO40-2, Vacuum Atmospheres, Hawthore, CA). All materials were added to the glove box through an isolated side chamber. This side chamber was reduced down to 30 mm Hg of vacuum after the samples were sealed inside and then refilled to ambient pressure with the dry argon from the glove box. This process was repeated three times before the samples were moved into the main chamber of the glove box. The catalyst dilutions were carried out using an analytical balance (Mettler-Toledo, Columbus, OH), which was inside the glove box.

A less rigorously controlled environment was used to prepare the less moisture sensitive materials. The samples of 2,6-*cis* with internal standard, naphthalene, dissolved in solvent were prepared in volumetric flasks in a controlled environment, 10 to 15% relative humidity, nitrogen-purged, positive-pressure, polyvinylchloride (PVC) glove box (Series 100, Terra Universal, Fullerton, CA). The nitrogen was passed through Drierite® (W.A. Hammond Drierite Company, Xenia, OH) before entering the glove box. Solvents were stored inside the nitrogen glove box. Silanised crimp-top GC sample vials (Agilent, Palo Alto, CA) were charged under ambient conditions with the 2,6-*cis*/naphthalene solution and solvent, then crimped. The catalyst solution was then syringed into this vial, and the sample was shaken and placed in the heating block auto-sampler on the GC.

5.2.1 Reactions Catalysed by Trifluoromethanesulphonic Acid

2,6-*cis* was treated with various concentrations of catalyst, all in a polar aprotic solvent, nitromethane (CH_3NO_2). Three catalyst solutions were prepared. Triflic acid (0.0134 g, 99+% obtained in a breakable glass vial) was diluted to a volume of 2.00 ml with nitromethane using a volumetric flask in the argon-purged glove box. The solution was transferred to an oven-dried, crimp-top GC vial prior to removal from the glove box, and labelled 136A. For the second catalyst solution, triflic acid (0.0053 g) was diluted to a volume of 2.00 ml with nitromethane using a volumetric flask in the argon-purged glove box. The solution was transferred to an oven-dried, crimp-top GC vial prior to removal from the glove box, and labelled 146A. For the third catalyst solution, triflic acid (0.0205 g) was diluted to a volume of 5.00 ml with nitromethane using a volumetric flask in the argon-purged glove box. The solution was transferred to an oven-dried, crimp-top GC vial prior to removal from the glove box, and labelled 154A.

Two 2,6-*cis* solutions were prepared. For the first solution, 2,6-*cis* (0.2811 g) and naphthalene (0.1162 g) were dissolved in nitromethane to a volume of 10.00 ml using a volumetric flask, and labelled 139B. For the second solution, 2,6-*cis* (0.7622 g) and naphthalene (0.3520 g) were dissolved in nitromethane to a volume of 25.00 ml using a volumetric flask, and labelled 147B.

The reactions were carried out in nitromethane at 30, 40, 50, 60, and 70°C. Table 5.1 lists the sample numbers, quantities, and concentrations.

30°C	136A		139B		CH_3NO_2		2,6-*cis*	Naphthalene	Triflic acid
Sample	ml	g	ml	g	ml	g	mol/ l	mol/ l	mol/ l
140-1	0.06	0.0685	0.50	0.5640	1.19	1.3476	1.90E-02	2.58E-02	1.54E-03
140-2	0.05	0.0563	0.50	0.5678	1.20	1.3608	1.91E-02	2.59E-02	1.27E-03
140-3	0.03	0.0339	0.50	0.5693	1.22	1.3840	1.92E-02	2.60E-02	7.62E-04
140-4	0.04	0.0447	0.50	0.5767	1.21	1.3790	1.93E-02	2.61E-02	9.98E-04
140-5	0.07	0.0786	0.50	0.5699	1.18	1.3458	1.91E-02	2.59E-02	1.76E-03
141-1	0.10	0.1123	0.50	0.5634	1.15	1.3022	1.90E-02	2.58E-02	2.54E-03
141-2	0.15	0.1688	0.50	0.5767	1.10	1.2498	1.93E-02	2.62E-02	3.78E-03

40°C	146A		147B		CH_3NO_2		2,6-*cis*	Naphthalene	Triflic acid
Sample	ml	g	ml	g	ml	g	mol/ l	mol/ l	mol/ l
148-3	0.08	0.0900	0.50	0.5577	1.17	1.3272	2.05E-02	3.10E-02	8.0E-04
148-4	0.07	0.0789	0.50	0.5593	1.18	1.3315	2.06E-02	3.12E-02	7.1E-04
149-1	0.10	0.1115	0.50	0.5624	1.15	1.3100	2.06E-02	3.11E-02	9.9E-04
149-2	0.09	0.1022	0.50	0.5639	1.16	1.3175	2.06E-02	3.12E-02	9.1E-04
149-3	0.12	0.1481	0.50	0.5548	1.13	1.2704	2.04E-02	3.09E-02	1.3E-03
150-1	0.11	0.1254	0.50	0.5616	1.14	1.2832	2.07E-02	3.13E-02	1.1E-03
150-2	0.13	0.1469	0.50	0.5562	1.12	1.2636	2.05E-02	3.11E-02	1.3E-03
150-3	0.14	0.1592	0.50	0.5702	1.11	1.2558	2.08E-02	3.16E-02	1.4E-03

50°C	146A		147B		CH_3NO_2		2,6-*cis*	Naphthalene	Triflic acid
Sample	ml	g	ml	g	ml	g	mol/ l	mol/ l	mol/ l
151-3	0.10	0.1149	0.50	0.5660	1.15	1.2995	2.072E-02	3.139E-02	1.0E-03
152-3	0.11	0.1258	0.50	0.5690	1.14	1.2880	2.081E-02	3.152E-02	1.1E-03
153-1	0.12	0.1360	0.50	0.5624	1.13	1.2925	2.048E-02	3.103E-02	1.2E-03
153-2	0.13	0.1479	0.50	0.5653	1.12	1.2748	2.062E-02	3.124E-02	1.3E-03

50°C	154A		147B		CH_3NO_2		2,6-*cis*	Naphthalene	Triflic acid
Sample	ml	g	ml	g	ml	g	mol/ l	mol/ l	mol/ l
159-2	0.07	0.0780	0.50	0.5701	1.18	1.3324	2.066E-02	3.130E-02	4.25E-04
159-3	0.06	0.0683	0.50	0.5630	1.19	1.3459	2.059E-02	3.119E-02	3.70E-04

60°C	154A		147B		CH_3NO_2		2,6-*cis*	Naphthalene	Triflic acid
Sample	ml	g	ml	g	ml	g	mol/ l	mol/ l	mol/ l
155-3	0.05	0.0579	0.50	0.5624	1.20	1.3535	2.066E-02	3.130E-02	8.01E-04
155-4	0.04	0.046	0.50	0.5613	1.21	1.3704	2.058E-02	3.118E-02	6.35E-04
156-1	0.03	0.0349	0.50	0.5621	1.22	1.3693	2.073E-02	3.140E-02	4.85E-04
160-3	0.055	0.0622	0.50	0.5701	1.195	1.3474	2.088E-02	3.163E-02	8.58E-04
160-4	0.06	0.0679	0.50	0.5706	1.19	1.3469	2.084E-02	3.157E-02	9.34E-04
2-1	0.055	0.0625	0.50	0.5598	1.195	1.3379	2.071E-02	3.137E-02	8.71E-04

70°C	154A		147B		CH_3NO_2		2,6-*cis*	Naphthalene	Triflic acid
Sample	ml	g	ml	g	ml	g	mol/ l	mol/ l	mol/ l
157-3	0.04	0.046	0.50	0.5708	1.21	1.3705	2.083E-02	3.155E-02	6.32E-04
158-1	0.05	0.0565	0.50	0.5709	1.20	1.3605	2.082E-02	3.155E-02	7.77E-04
3-1	0.055	0.0596	0.50	0.5687	1.195	1.3510	2.083E-02	3.156E-02	8.23E-04
3-2	0.045	0.0508	0.50	0.5652	1.205	1.3653	2.069E-02	3.134E-02	7.00E-04
3-3	0.048	0.0535	0.50	0.5600	1.202	1.3570	2.061E-02	3.122E-02	7.42E-04
3-4	0.058	0.0652	0.50	0.5740	1.192	1.3490	2.093E-02	3.171E-02	8.96E-04

Table 5.1 Interconversion samples catalysed by trifluoromethanesulphonic acid prepared for GC kinetic analysis

The conversion from 2,6-*cis* to an equimolar mixture of the 2,6-*cis* and 2,6-*trans* cyclosiloxane isomers was followed by GC. Groups of tables in Appendix A list the GC data at various catalyst concentrations for each temperature. Where #NUM! is listed in place of a value, it indicates that the calculation was attempting to take the natural log of a negative number.

Each group of tables in Appendix A is accompanied by an associated group of figures that show the interconversion rate (the amount of 2,6-*trans* that is formed over time and the loss of 2,6-*cis*). The initial amount of 2,6-*trans* is 0, and the reaction proceeds to an approximate 50:50 mixture of the 2,6-*cis*:2,6-*trans* isomers (49.8% *cis*:50.2% *trans).*

5.2.1.1 Reactions Catalysed by Trifluoromethanesulphonic Acid with DBMP

2,6-*cis* was treated with various concentrations of aluminium trifluoromehtnaesulphonic acid catalyst, all in a polar aprotic solvent, nitromethane (CH_3NO_2). Triflic acid (0.0127 g) was diluted to a volume of 2.00 ml with nitromethane using a volumetric flask in the nitrogen-purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, labelled 22A1, and used as catalyst for all the samples. The proton sponge DBMP (2,6-di-*tert*-butyl-4-methylpyridine) (0.0657g) was diluted to a volume of 5.00 ml with nitromethane using a volumetric flask in the nitrogen-purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, labelled 22C, and used as catalyst for samples 22-2, 22-3, and 23-1. 2,6-*cis* (0.7667 g) and naphthalene (0.29173 g) were dissolved in nitromethane to a volume of 25.00 ml using a volumetric flask, and labelled 2B.

The reactions were carried out in nitromethane at 40°C. Table 5.2 lists the sample numbers, quantities, and concentrations.

40°C	22A1		22C		2B		CH_3NO_2		2,6-*cis*	Naphthalene	CF_3SO_3H	DBMP
Sample	ml	g	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l	mol/l
22-1	0.05	0.0537			0.50	0.5700	1.20	1.3663	2.09E-02	2.61E-02	1.14E-03	
22-2	0.05	0.0562	0.02	0.0232	0.50	0.5693	1.18	1.3406	2.09E-02	2.61E-02	1.20E-03	7.46E-04
22-3	0.05	0.0569	0.04	0.0454	0.50	0.5667	1.16	1.3150	2.08E-02	2.60E-02	1.21E-03	1.46E-03
23-1	0.10	0.1125	0.02	0.0234	0.50	0.5680	1.13	1.2839	2.08E-02	2.60E-02	2.40E-03	7.53E-04

Table 5.2 Interconversion/ polymerisation samples catalysed by aluminium triflate prepared for GC kinetic analysis

5.2.2 Reactions Catalysed by Methanesulphonic Acid

2,6-*cis* was treated with various concentrations of methanesulphonic acid catalyst, all in a polar aprotic solvent, nitromethane (CH_3NO_2). Two catalyst solutions were prepared. For one group of samples, methanesulphonic acid (0.0975 g, 99.5+% obtained in a breakable glass vial) was diluted to a volume of 5.00 ml with nitromethane using a volumetric flask in the argon-purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, labelled 13A, and used as catalyst for samples 13-2, 13-3, 14-1, and 14-2. For all other samples, methanesulphonic acid (0.1005 g) was diluted to a volume of 5.00 ml with nitromethane using a volumetric flask, as above. This solution was also placed in an oven-dried, crimp-top vial before removal from the argon-purged glove box, and labelled 5A. One 2,6-*cis* solution was prepared. 2,6-*cis* (0.7667 g) and naphthalene (0.2917 g) were dissolved in nitromethane to a volume of 25.00 ml using a volumetric flask, and labelled 2B.

The reactions were carried out in nitromethane at 40, 50, 60, and 70°C. Table 5.3 lists the sample numbers, quantities, and concentrations.

40°C	5A		2B		CH_3NO_2		2,6-*cis*	Naphthalene	Methanesulphonic acid
Sample	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
13-1	0.20	0.2273	0.50	0.5661	1.00	1.1957	2.08E-02	2.59E-02	2.39E-02

40°C	13A		2B		CH_3NO_2		2,6-*cis*	Naphthalene	Methanesulphonic acid
Sample	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
13-2	0.20	0.2208	0.50	0.5686	1.05	1.1868	2.10E-02	2.62E-02	2.27E-02
13-3	0.18	0.2042	0.50	0.5654	1.07	1.2116	2.08E-02	2.60E-02	2.09E-02
14-1	0.16	0.1828	0.50	0.5722	1.09	1.2361	2.10E-02	2.62E-02	1.86E-02
14-2	0.22	0.249	0.50	0.5641	1.03	1.1698	2.07E-02	2.59E-02	2.55E-02

50°C	5A		2B		CH_3NO_2		2,6-*cis*	Naphthalene	Methanesulphonic acid
Sample	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
11-1	0.20	0.2232	0.50	0.5621	1.05	1.1876	2.08E-02	2.59E-02	2.37E-02
11-2	0.18	0.2034	0.50	0.5694	1.07	1.2094	2.10E-02	2.61E-02	2.15E-02
11-3	0.20	0.2268	0.50	0.5636	1.05	1.1951	2.07E-02	2.58E-02	2.39E-02
12-1	0.22	0.2515	0.50	0.5641	1.03	1.1725	2.07E-02	2.58E-02	2.65E-02
12-2	0.16	0.1824	0.50	0.5654	1.09	1.2379	2.08E-02	2.59E-02	1.92E-02
12-3	0.14	0.1504	0.50	0.5685	1.11	1.2531	2.10E-02	2.62E-02	1.60E-02

60°C	5A		2B		CH_3NO_2		2,6-*cis*	Naphthalene	Methanesulphonic acid
Sample	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
8-1	0.20	0.2272	0.50	0.5643	1.05	1.1968	2.07E-02	2.58E-02	2.39E-02
8-2	0.16	0.1834	0.50	0.5623	1.09	1.2464	2.06E-02	2.57E-02	1.93E-02
8-3	0.24	0.2741	0.50	0.5660	1.01	1.1524	2.07E-02	2.59E-02	2.88E-02
9-1	0.18	0.2056	0.50	0.5642	1.07	1.2079	2.08E-02	2.60E-02	2.17E-02
9-2	0.14	0.1597	0.50	0.5634	1.11	1.2668	2.07E-02	2.58E-02	1.68E-02
9-3	0.12	0.1368	0.50	0.5742	1.13	1.2792	2.10E-02	2.63E-02	1.44E-02
9-4	0.10	0.114	0.50	0.5688	1.15	1.3019	2.09E-02	2.61E-02	1.20E-02
10-1	0.22	0.2489	0.50	0.5660	1.03	1.1707	2.08E-02	2.59E-02	2.62E-02

70°C	5A		2B		CH_3NO_2		2,6-*cis*	Naphthalene	Methanesulphonic acid
Sample	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
5-1	0.30	0.3415	0.50	0.5607	0.95	1.0858	2.06E-02	2.57E-02	3.59E-02
5-2	0.20	0.2277	0.50	0.5595	1.05	1.1880	2.07E-02	2.58E-02	2.41E-02
5-3	0.10	0.1143	0.50	0.5555	1.15	1.2967	2.06E-02	2.57E-02	1.22E-02
6-1	0.16	0.1817	0.50	0.5617	1.09	1.2317	2.07E-02	2.59E-02	1.92E-02
6-2	0.14	0.1605	0.50	0.5653	1.11	1.2548	2.08E-02	2.60E-02	1.69E-02
6-3	0.12	0.138	0.50	0.5580	1.13	1.2730	2.07E-02	2.58E-02	1.47E-02
7-1	0.18	0.2051	0.50	0.5648	1.07	1.2123	2.08E-02	2.59E-02	2.16E-02
7-2	0.22	0.2528	0.50	0.5625	1.03	1.1741	2.06E-02	2.57E-02	2.66E-02
7-3	0.24	0.2732	0.50	0.5643	1.01	1.1514	2.07E-02	2.58E-02	2.87E-02

Table 5.3 Interconversion samples catalysed by methanesulphonic acid prepared for GC kinetic analysis

The conversion from 2,6-*cis* to an equimolar mixture of the 2,6-*cis* and 2,6-*trans* cyclics was followed by GC. Groups of tables in Appendix B list the GC data at various catalyst concentrations for each temperature. Where #NUM! is listed in place of a value, it indicates that the calculation was attempting to take the natural log of a negative number.

Each group of tables in Appendix B is accompanied by an associated group of figures that show the interconversion rate (the amount of 2,6-*trans* that is formed over time and the loss of 2,6-*cis*). The initial amount of 2,6-*trans* is 0, and the reaction proceeds to an approximate 50:50 mixture of the 2,6-*cis*:2,6-*trans* isomers (49.8% *cis*:50.2% *trans)*. The final group of figures in Appendix B detail the polymerisation rate

for each reaction.

5.2.3 Reactions Catalysed by Iron Chloride

2,6-*cis* was treated with two concentrations of $FeCl_3$ catalyst, both in a polar aprotic solvent, nitromethane (CH_3NO_2). Iron chloride, a solid Lewis acid (0.0144 g, 99+% obtained in a breakable 1 g glass vial), was diluted to a volume of 10.00 ml with nitromethane using a volumetric flask in the nitrogen-purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, and labelled 87A. 2,6-*cis* (0.7558 g) and naphthalene (0.7693 g) were dissolved in nitromethane to a volume of 25.00 ml using a volumetric flask, and labelled 87B.

The reactions were carried out in nitromethane at 40, 50, 60, and 70°C. Table 5.4 lists the sample numbers, quantities, and concentrations.

40°C	87A		87B		CH_3NO_2		2,6-*cis*	Naphthalene	$FeCl_3$
Sample	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
94-1	0.15	0.17	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
94-2	0.10	0.11	0.50	0.5635	1.15	1.2961	2.05E-02	6.86E-02	5.07E-04
50°C	87A		87B		CH_3NO_2		2,6-*cis*	Naphthalene	$FeCl_3$
Sample	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
92-1	0.15	0.17	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
92-2	0.15	0.11	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
93-1	0.10	0.11	0.50	0.5635	1.15	1.2961	2.05E-02	6.86E-02	5.07E-04
60°C	87A		87B		CH_3NO_2		2,6-*cis*	Naphthalene	$FeCl_3$
Sample	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
90-1	0.15	0.17	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
90-2	0.15	0.17	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
90-3	0.15	0.17	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
90-4	0.15	0.17	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
91-1	0.10	0.11	0.50	0.5635	1.15	1.2961	2.05E-02	6.86E-02	5.07E-04
91-2	0.10	0.11	0.50	0.5635	1.15	1.2961	2.05E-02	6.86E-02	5.07E-04
70°C	87A		87B		CH_3NO_2		2,6-*cis*	Naphthalene	$FeCl_3$
Sample	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
88-1	0.15	0.17	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
88-2	0.15	0.17	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
88-3	0.15	0.17	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
88-4	0.15	0.17	0.50	0.5635	1.10	1.2397	2.05E-02	6.86E-02	7.61E-04
89-1	0.10	0.11	0.50	0.5635	1.15	1.2961	2.05E-02	6.86E-02	5.07E-04
89-2	0.10	0.11	0.50	0.5635	1.15	1.2961	2.05E-02	6.86E-02	5.07E-04
89-3	0.10	0.11	0.50	0.5635	1.15	1.2961	2.05E-02	6.86E-02	5.07E-04
89-4	0.10	0.11	0.50	0.5635	1.15	1.2961	2.05E-02	6.86E-02	5.07E-04

Table 5.4 Interconversion samples catalysed by iron chloride prepared for GC kinetic analysis (calculations for grams are based on volume, where d (g/ml) of nitromethane = 1.127)

The conversion from 2,6-*cis* to an equimolar mixture of the 2,6-*cis* and 2,6-*trans* cyclosiloxanes were followed by GC. Groups of tables in Appendix C list the GC data for two concentrations of $FeCl_3$ for each temperature. Where #NUM! is listed in place of a value, it indicates that the calculation was attempting to take the natural log of a negative number.

Each group of tables in Appendix C is accompanied by an associated group of figures that show the interconversion rate (the amount of 2,6-*trans* (or 2,6-*cis* when 2,6-*cis* was the starting material) that is formed over time and the loss of 2,6-*cis* (or 2,6-*trans* when 2,6-*cis* was the starting material)). The initial amount of 2,6-*trans* is 0, and the reaction proceeds to an approximate 50:50 mixture of the 2,6-*cis*:2,6-*trans* isomers (49.8% *cis*:50.2% *trans)*.

The GC run time of 18 minutes dictates the frequency of data points. Crucial data will be missed if the reaction is mostly complete during this time (<20 minutes). This is common at higher temperatures and or higher catalyst concentrations, as the reactions proceed more quickly. Several samples of the same formulation were prepared in order to avoid this complication. The samples were held at temperature for varying amounts of time prior to injection into the GC to delay the first data point (e.g. 5, 10, 15 minutes). The results of various samples evaluated under the same conditions are combined to give a more complete data set (e.g. Table C.9 with samples 88-1, 88-2, 88-3, and 88-4). Where more than one sample label is indicated in the results, this staggered approach was used.

5.2.3.1 Reactions of 2,6-cis versus 2,6-trans Catalysed by Iron Chloride

2,6-*cis* or 2,6-*trans* was treated with $FeCl_3$ catalyst, both in a polar aprotic solvent,

nitromethane (CH_3NO_2). Iron chloride, (0.0145 g, 99+% obtained in a breakable 1 g glass vial), was diluted to a volume of 10.00 ml with nitromethane using a volumetric flask in the nitrogen-purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, and labelled 105A. 2,6-*cis* (0.7558 g) and naphthalene (0.7693 g) were dissolved in nitromethane to a volume of 25.00 ml using a volumetric flask, and labelled 87B. 2,6-*trans* (0.71715 g) and naphthalene (0.0993 g) were dissolved in nitromethane to a volume of 5.00 ml using a volumetric flask, and labelled 97B.

The reactions were carried out in nitromethane at 60°C. Table 5.5 lists the sample numbers, quantities, and concentrations.

60°C	105A		87B		97B		CH_3NO_2		2,6-*cis*	2,6-*trans*	Naphthalene	$FeCl_3$
Sample	ml	g	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l	mol/l
105-1	0.10	0.1127	0.50	0.5635			1.15	1.2961	2.05E-02		6.86E-02	5.52E-04
105-2	0.10	0.1127			0.50	0.5635	1.15	1.2961		2.33E-02	4.43E-02	5.52E-04

Table 5.5 Interconversion samples catalysed by iron chloride prepared for GC kinetic analysis (calculations for grams are based on volume, where d (g/ml) of nitromethane = 1.127)

5.2.3.2 Reactions Catalysed by Iron Chloride with Water

2,6-*cis* was treated with $FeCl_3$ catalyst in a polar aprotic solvent, nitromethane (CH_3NO_2). Iron chloride, a solid Lewis acid (0.0010 g, 99+% obtained in a breakable 1 g glass vial), was diluted to a volume of 2.00 ml with nitromethane using a volumetric flask in the nitrogen-purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, and labelled 120A. 2,6-*cis* (0.0938 g) and naphthalene (0.0332 g) were dissolved in nitromethane to a volume of 5.00 ml using a volumetric flask, and labelled 120B. A third solution was prepared with 4.00 µl of distilled water diluted to a volume of 10.00 ml with nitromethane using a volumetric flask, and was labelled 120°C (400 ppm water).

The reactions were carried out in nitromethane at 60°C. Table 5.6 lists the sample

numbers, quantities, and concentrations.

60°C	120A		120B		120C		CH_3NO_2		2,6-*cis*	Naphthalene	$FeCl_3$
Sample	ml	g	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
122-1	0.40	0.4508	0.50	0.5635	0.00	0	0.85	0.9580	2.05E-02	6.86E-02	7.1E-04
122-2	0.40	0.4508	0.50	0.5635	0.45	0.5072	0.40	0.4508	2.77E-02	9.23E-02	7.1E-04
122-3	0.40	0.4508	0.50	0.5635	0.85	0.9580	0.00	0.0000	3.99E-02	1.33E-01	7.1E-04
122-4	0	0	0.50	0.5635	0.00	0	1.25	1.4088	2.05E-02	6.86E-02	0.0E+00

Table 5.6 Interconversion samples catalysed by iron chloride and water prepared for GC kinetic analysis (calculations for grams are based on volume, where d (g/ml) of nitromethane = 1.127)

Table C.11 in Appendix C shows the GC results and calculations from the samples prepared according to Table 5.6.

2,6-*cis* was treated with $FeCl_3$ catalyst in a polar aprotic solvent, nitromethane (CH_3NO_2). Iron chloride, (0.0507 g, 99+% obtained in a breakable 1 g glass vial), was diluted to a volume of 25.00 ml with nitromethane using a volumetric flask in the argon-purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, and labelled 135A. 2,6-*cis* (0.2760 g) and naphthalene (0.1298 g) were dissolved in nitromethane to a volume of 5.00 ml using a volumetric flask, and labelled 129B.

The reactions were carried out in nitromethane at 60°C. Table 5.7 lists the sample numbers, quantities, and concentrations.

60°C	135A		129B		Water		CH_3NO_2		2,6-*cis*	Naphthalene	$FeCl_3$
Sample	ml	g	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
135-2	0.09	0.0979	0.50	0.5706	0.0010	0.0009	1.16	1.3126	1.891E-02	2.92E-02	6.18E-04
135-3	0.09	0.0983	0.50	0.5681	0.0030	0.0030	1.16	1.3124	1.885E-02	2.91E-02	6.21E-04

Table 5.7 Interconversion samples catalysed by iron chloride and water prepared for GC kinetic analysis

5.2.4 *Reactions Catalysed by Sulphuric Acid*

2,6-*cis* was treated with various concentrations of sulphuric acid catalyst, all in a polar aprotic solvent, nitromethane (CH_3NO_2). Sulphuric acid (0.0208 g, 99.999%) was diluted to a volume of 2.00 ml with nitromethane using a volumetric flask in the nitrogen-purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, labelled 121A, and used as catalyst for samples 121-1, and 121-2.

The reactions were carried out in nitromethane at 60°C. Table 5.8 lists the sample numbers, quantities, and concentrations.

60°C	121A		120B		CH_3NO_2		2,6-*cis*	Naphthalene	H_2SO_4
Sample	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l
121-1	0.002	0.0023	0.50	0.5635	1.23	1.3862	1.28E-02	1.48E-02	1.21E-03
121-2	0.10	0.1127	0.50	0.5635	1.15	1.2961	1.28E-02	1.48E-02	6.06E-03

Table 5.8 Interconversion/ polymerisation samples catalysed by sulphuric acid prepared for GC kinetic analysis (calculations for grams are based on volume, where d (g/ml) of nitromethane = 1.127)

5.2.5 *Reactions Catalysed by Aluminium Trifluoromethanesulphonic Acid*

2,6-*cis* was treated with various concentrations of aluminium trifluoromehtnaesulphonic acid catalyst, all in a polar aprotic solvent, nitromethane (CH_3NO_2). Aluminium triflate (0.0344 g) was diluted to a volume of 5.00 ml with nitromethane using a volumetric flask in the nitrogen-purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, labelled 15A, and used as catalyst for all the samples. The proton sponge DBMP (2,6-di-*tert*-butyl-4-methylpyridine) (0.0047g) was diluted with 1.0590g of the solution 15A in the nitrogen-purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, labelled 15A2, and used as catalyst for samples 15-2, 17-2, and 17-3. The proton sponge DBMP (2,6-di-*tert*-butyl-4-methylpyridine) (0.0029g) was diluted to a volume of 1.00 ml with nitromethane using a volumetric flask in nitrogen-

purged glove box. The solution was transferred to an oven-dried, crimp-top vial prior to removal from the glove box, labelled 15C, and used as a proton trap for samples 16-1, and 16-2. 2,6-*cis* (0.7667 g) and naphthalene (0.29173 g) were dissolved in nitromethane to a volume of 25.00 ml using a volumetric flask, and labelled 2B.

The reactions were carried out in nitromethane at 40°C. Table 5.9 lists the sample numbers, quantities, and concentrations.

40°C	15A2		15A		15C		2B		CH_3NO_2		2,6-*cis*	Naphthalene	$Al(SO_3CF_3)_3$	DBMP
Sample	ml	g	ml	g	ml	g	ml	g	ml	g	mol/l	mol/l	mol/l	mol/l
15-2	0.10	0.1134					0.50	0.5651	1.15	1.3022	2.08E-02	2.60E-02	8.27E-04	1.3E-03
16-1			0.20	0.2296	0.04	0.0454	0.50	0.5661	1.05	1.1956	2.03E-02	2.53E-02	1.64E-03	1.6E-04
16-2			0.20	0.2284	0.06	0.0669	0.50	0.5630	1.05	1.1862	2.01E-02	2.51E-02	1.62E-03	2.3E-04
17-1			0.20	0.2258			0.50	0.5727	1.05	1.1933	2.10E-02	2.62E-02	1.65E-03	
17-2	0.05	0.0562	0.15	0.1693			0.50	0.5680	1.05	1.1912	2.09E-02	2.61E-02	1.65E-03	6.9E-04
17-3	0.15	0.1700	0.05	0.0559			0.50	0.5607	1.05	1.1871	2.07E-02	2.59E-02	1.66E-03	2.1E-04

Table 5.9 Interconversion/ polymerisation samples catalysed by aluminium triflate prepared for GC kinetic analysis

Solution 15C (0.04 ml) was added to sample 16-1 after 1 hr 33 min of analysis at 40°C. Solution 15C (0.06 ml) was added to sample 16-2 after 45 min of analysis at 40°C.

5.2.6 Reactions for ^1H NMR Proton Sponge-Aluminium Triflate Complex

The proton sponge-Lewis acid complex reactions were carried out in duetrated nitromethane at room temperature. The samples were prepared under atmospheric conditions in a sample vial and transferred into an NMR tube. Table 5.10 lists the sample numbers, quantities, and concentrations.

	$Al(SO_3CF_3)_3$	CF_3SO_3H	Proton Sponge ($C_{14}H_{18}N_2$)	CD_3NO_2		$Al(SO_3CF_3)_3$	CF_3SO_3H	Proton Sponge ($C_{14}H_{18}N_2$)
Sample	g	g	g	g	mL	mol/L	mol/L	mol/L
63-1	0.3204			8.2325	9.2780	7.3E-05	0.0E+00	0.0E+00
63-2			0.0864	4.3399	4.8911	0.0E+00	0.0E+00	8.2E-05
63-3	0.0224		0.0420	4.4956	5.0665	9.3E-06	0.0E+00	3.9E-05
63-4		0.5343		7.1006	8.0024	0.0E+00	4.4E-04	0.0E+00
63-5		0.2512	0.0962	3.3385	3.7625	0.0E+00	4.4E-04	1.2E-04

Table 5.10 Proton sponge complex samples prepared for NMR analysis

Only the top liquid layer was analysed as the high concentration of aluminium

triflate used for the NMR samples were not completely soluble in nitromethane-d_3.

5.3 Measurement of Water Content by Karl Fischer Titration

Karl Fischer titration of the solvents, reactants, and some of the acids was carried out to determine the amount of water inherently present in these materials (Table 5.11). This technique is a volumetric titration commonly used to accurately determine the amount of water present in various substances. A Karl Fischer coulometer (Model DL37, Mettler-Toledo Columbus, OH) was used with Hydranal® titrant reagents (Riedel-de Haën, a Sigma-Aldrich company, St. Louis, MO). (Test noise = 5 ppm.)

Material	Mass (g)	Water (ppm)
nitromethane	0.7272	49.230
	0.8691	52.353
$FeCl_3$ (0.0034 g) in nitromethane (2 ml)	0.8803 (solution)	131.09
	0.5290 (solution)	133.65
nitrobenzene	0.9536	28.104
2-nitropropane	0.6819	155.59
nitrocyclopentane	0.5052	945.96
1-nitrobutane	0.4598	248.80
acetonitrile	0.3173	80.050
dimethylsulphoxide	0.6826	190.16
n-pentane (solvent for proton sponge)	—	27
proton sponge: 2,6-di-*tert*-butyl-4-methylpyridine (0.0615 g) in n-pentane (10 ml)	—	25

Table 5.11 Water content in solvents and reactants determined by Karl Fischer titration

5.4 Measurement of Kinetic Data by Gas Chromatography

A Hewlett-Packard 6890 gas chromatograph (Agilent, Palo Alto, CA) equipped with a Leap auto-sampler (CTC Analytics, Zwingen, Switzerland) was used to obtain the kinetic data in these experiments, as well as typical gas chromatograms. The Leap auto-

sampler was programmed to rinse the 1 µl syringe according to the following conditions set up in the Cycle Composer programme: two pre-cleans with 1 µl of solvent 1 (toluene); followed by two pre-cleans with 1 µl of solvent 2 (CH_3NO_2); followed by one pre-clean with sample (set at 0.1 µl). The syringe was then filled and emptied with sample five times to remove air, using a filling speed of 5 µl/s, with a 300 ms pull-up delay and an injection speed of 50 µl/s.

Injection of 0.1 µl of sample was followed by two post-cleans of the syringe with solvent 1 and two with solvent 2. The samples were injected into the GC, which contained a tapered pre-column followed by an Agilent DB-5 (5% phenyl methyl siloxane liquid phase) capillary column 30 m x 250 µm x 0.25 µm nominal (Agilent, Palo Alto, CA). More retention of the 2,6 isomers was observed on the DB-5 column versus a DB-1/ ZB-1 (100% PDMS) column. The use of the DB-5 column resulted in better separation and baseline resolution of the 2,6-*trans* and 2,6-*cis* isomers as well as the 2,4 isomers.

The following ramp conditions were used prior to the sample entering the flame ionisation detector (FID):

Injection temperature = 250°C

Detector temperature = 275°C

Initial oven temperature = 80°C, hold 1 minute

Ramp 20°C/minute to 220°C, hold 3 minutes

Ramp 20°C/minute to 250°C, hold 5.5 minutes

Total run = 18 minutes

Split = 150:1

The initial oven temperature was held at a temperature lower than the boiling point of the solvent (bp of nitromethane = 101°C) to avoid condensation on the front of the column.

A Thermolyne-type 16500 aluminium block Dri-bath (Thermolyne/Barnstead, Dubuque, IA) was purchased with temperature uniformity ±0.5°C, temperature stability ±0.1°C, and an operating range of ambient +5°C to 110°C. This dry bath was placed on the GC and aligned so the auto-sampler could take samples from the bath, see Figure 5.1.

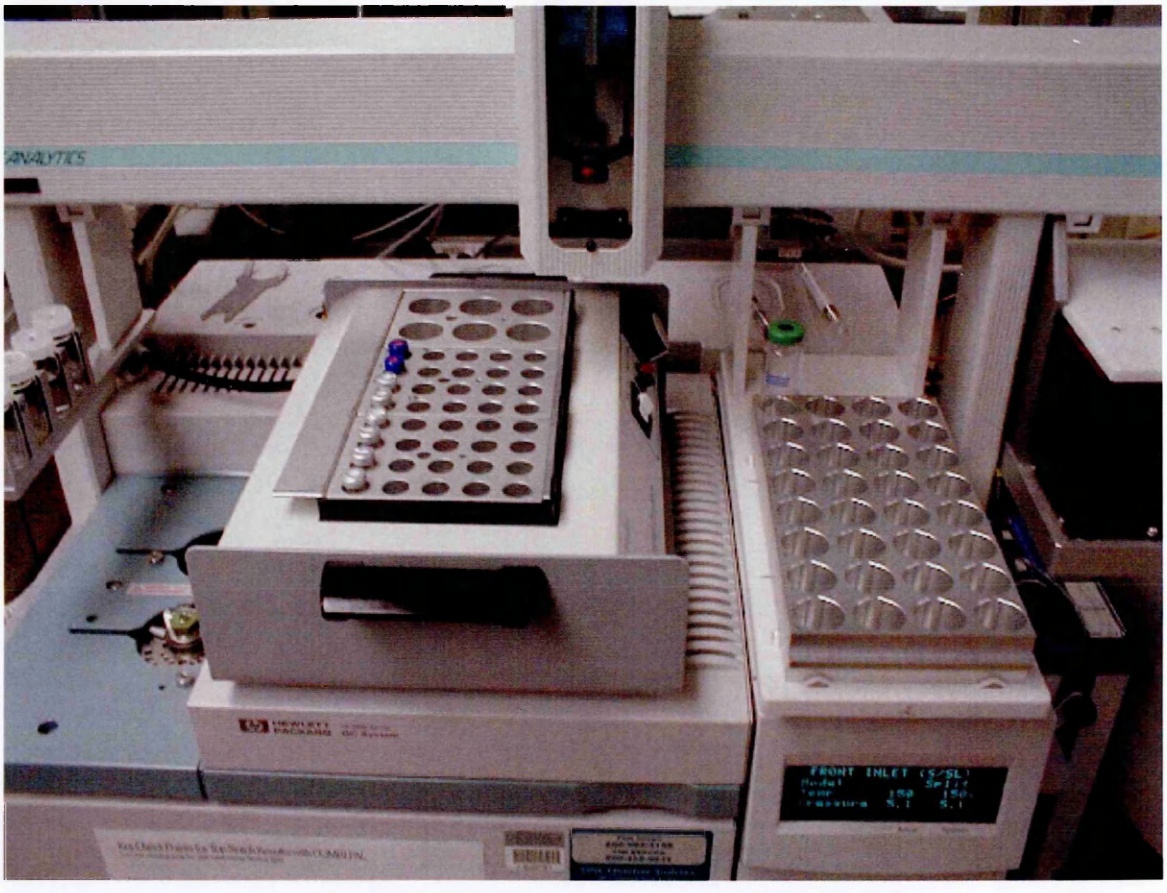


Figure 5.1 Dry bath heating block placed atop the GC equipped with an auto-sampler

A dry bath temperature study was performed with a thin thermocouple probe on the aluminium block and compared with the temperature of samples of water in vials located at various locations in the aluminium block. At 70°C there was 0.5°C difference between the centre of the vial and the inside wall, at 60°C a 0.4°C difference was observed, while at 50°C only 0.1°C difference was noted. Also, at 80°C there was 2.5 to 3°C difference in temperature between the centre of the vial containing water and the aluminium block, while only ~0.5°C difference was observed at 40°C. The maximum

temperature used in the kinetic studies was 70°C. No measurable difference in temperature was observed with sample vials located in the different positions of the aluminium block. The water temperature measured in the centre of the vial is the temperature used in the kinetic studies.

5.4.1 Determination of Internal Standard and Response Factor

Calibrations of the GC with respect to our compounds of interest are necessary in order to obtain quantitative chromatographic analyses. This is because the FID detector does not respond equally to all compounds. Both the injection volume and the rate of injection can add error. The use of an auto-sampler, like the one described above, will reduce those errors. However, an internal standard method will avoid these issues by comparing the ratio of GC peak areas of each compound to those of the internal standard.

Several siloxanes were evaluated as internal standards, but their reactivity with the acid catalysts precluded their use. Naphthalene, an organic compound that elutes close to the 2,6 isomers, was selected as the internal standard. In order to determine the response factor between the internal standard and the starting material, a series of dilutions was prepared and analysed. A solution containing 2,6-*cis* (0.7558 g) and naphthalene (0.7693 g) was diluted to 25 ml with nitromethane in a volumetric flask, which was labelled 87B. Solution 87B was systematically diluted further with nitromethane. Gas chromatograms were obtained and are plotted as a function of concentration in Figure 5.2.

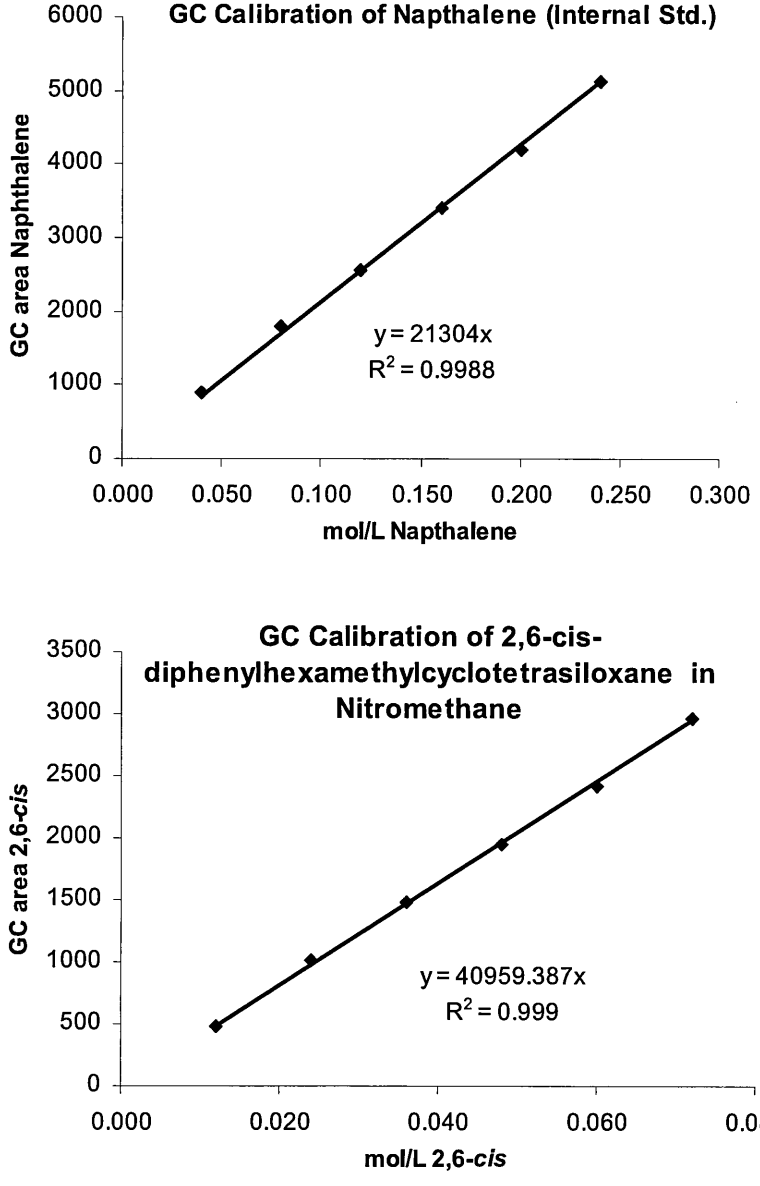


Figure 5.2 GC calibration of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane and naphthalene in nitromethane

The plots in Figure 5.2 fit very well to the best-fit line in each graph which bisects the origin. The R_f (response factor) was calculated to be 1.90 between naphthalene as the internal standard and 2,6-*cis* as the analyte of interest according to $R_f = (C_y A_x)/(C_x A_y)$, where C is concentration, A is area, x is the analyte of interest (2,6-*cis*), and y is internal standard (naphthalene), see Table 5.12.[101] This same formula will be used to calculate concentration of analyte, now that the R_f is known, using the equation $C_x = (C_y A_x)/(R_f A_y)$.

Sample	Dilution (solution 87B in CH3NO2)	mol/l naphthalene	mol/l 2,6-*cis*	GC area naphthalene	GC area 2,6-*cis*	area 2,6-*cis*/ naphthalene	Response Factor
87-1	0.25ml 87B/ 1.25mL CH3NO2	0.0400	0.0120	887	486	0.5476	1.828
87-2	0.50ml 87B/ 1.00mL CH3NO2	0.0800	0.0240	1804	1018	0.5641	1.883
87-3	0.75ml 87B/ 0.75mL CH3NO2	0.1200	0.0360	2562	1480	0.5778	1.929
87-4	1.00ml 87B/ 0.50mL CH3NO2	0.1600	0.0479	3403	1947	0.5722	1.910
87-5	1.25ml 87B/ 0.25mL CH3NO2	0.2001	0.0599	4208	2414	0.5738	1.916
87-6	all 87B	0.2401	0.0719	5123	2974	0.5805	1.938
Sum							11.405
Average							**1.901**

Table 5.12 GC calibration of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane and naphthalene in nitromethane

Other compounds were attempted as internal standards. 3,3-Diphenyl-1,1,1,5,5,5-hexamethyltrisiloxane treated with the iron chloride catalyst and thus could not be used as an internal standard. Based on these results, and a few other attempts with phenyl-substituted siloxanes, a siloxane internal standard was not used. Hexadecane was also evaluated as an internal standard, but it does not elute close to the desired 2,6-*cis* or 2,6-*trans* peaks. Thus, larger organic compounds were evaluated. Cyclic compounds were the natural choice to increase the retention on the column similar to the phenyl-substituted siloxane under evaluation. A sample of 1,5-cyclooctadiene drops into nitromethane like oil does into water, but mixes in and does not separate. 1-Phenyldodecane and *cis*, *cis*-1,3-cyclooctadiene are both insoluble in nitromethane. Naphthalene is soluble, dissolves easily in nitromethane, and elutes reasonably close (5.4 minutes) to the cyclosiloxanes under review, 2,6-*cis* (10.2 minutes) and 2,6-*trans* (10.4 minutes).

5.4.2 Comparison of Treated and Untreated GC Vials

The GC vial surface was examined in an attempt to determine the many causes of the premature consumption of the catalyst. It was postulated that untreated glass vials would provide a source of moisture, and possibly protons from silanol and adsorbed

moisture, which could alter the catalyst. In order to test this hypothesis, three types of vials were evaluated. The first vial was purchased from Agilent and did not have any treatment. The second was the same as the first, only it was treated in our laboratory with hexamethyldisilazane (HMDZ). The treatment is described in Section 5.4.2.1 GC Vial Treatment. The third vial was a silanised vial purchased from Agilent pre-treated, and used as received. A reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane with triflic acid in nitromethane solvent at 30°C was used as the test case for the three types of vials. The interconversion reaction proceeds to the 50:50 *cis*:*trans* equilibrium as expected, but the untreated vial lags behind, see Figure 5.3.

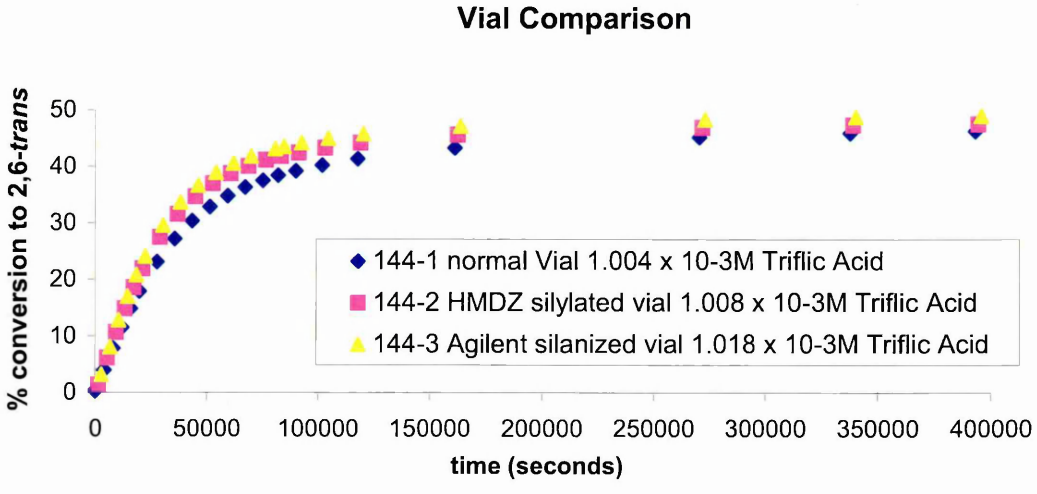


Figure 5.3 Interconversion of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane to the 2,6-*trans* isomer catalysed by trifluoromethanesulphonic acid in nitromethane at 30°C using treated and untreated vials

The untreated vial (144-1 in Figure 5.3) was consuming the catalyst, at least faster than the treated vials. The rate of the reaction was calculated with the same techniques used with the other triflic acid reactions in Chapter 2, and is shown in Figure 5.4.

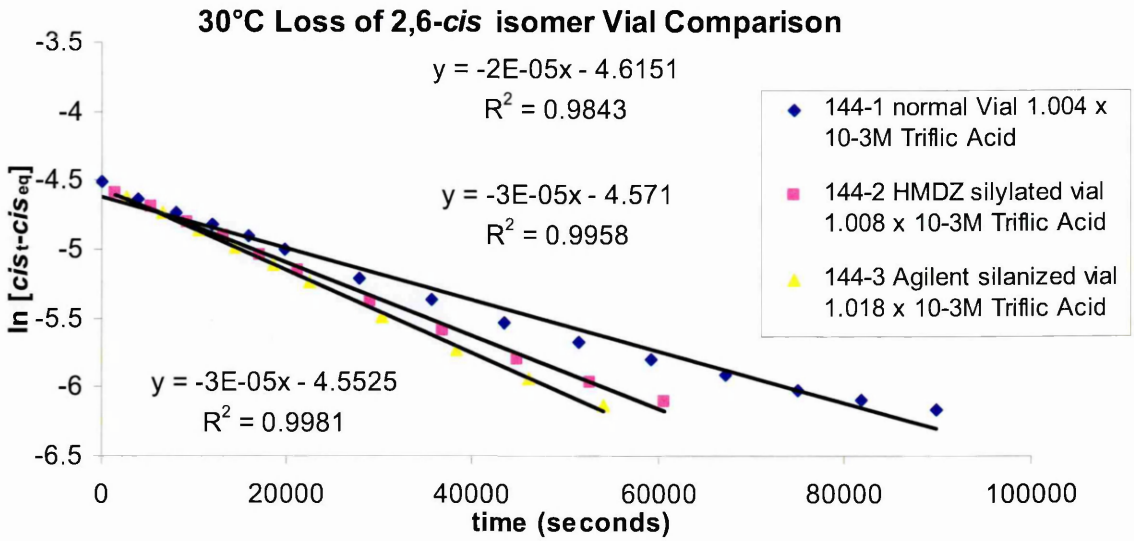


Figure 5.4 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.0 mM trifluoromethanesulphonic acid in nitromethane at 30°C

The data are tabulated in Table 2.5. The last column displays the rate of the reaction divided by the concentration of acid used. This should normalize any small discrepancies caused by the variation in triflic acid concentration. These data again show that treatment of the vials increased the reaction rate substantially.

Sample	[triflic acid] (mM)	[2,6-*cis*] (mM)	*k* (mol/ l s)	*k*/ [triflic acid] (1/s)
144-1 GC vial	1.00	19.0	1.9E-05	1.00E-03
144-2 HMDZ silylated vial	1.01	19.2	2.7E-05	1.41E-03
144-3 Agilent pre-treated silanised vial	1.02	19.2	3.0E-05	1.56E-03

Table 5.13 Comparison of reaction rate constants calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by trifluoromethanesulphonic acid in nitromethane at 30°C using treated and untreated GC vials

5.4.2.1 GC Vial Treatment

Two millilitre gas chromatography vials (Agilent, Palo Alto, CA)) were cleaned by rinsing with acetone (three times), followed by ethanol (three times), and dried at 110°C for 2 hours. Each vial was exposed to a solution of 2.00 ml hexamethyldisilazane (Dow

Corning Corporation, Midland, MI) and 0.10 ml acetic acid (Fisher Scientific, Pittsburgh, PA) overnight to treat the glass surface. The vials were rinsed again with ethanol (three times) and stored at 110°C until use.

Chapter Six

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6 References

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Appendix A

Data for Interconversion Reactions Catalysed by

Trifluoromethanesulphonic Acid

Appendix A. Data for Interconversion Reactions Catalysed by Trifluoromethanesulphonic Acid

140-1 (1.54 mM Triflic Acid)	time (sec)	0	64	1375	2688	4001	5315	6629	7943	9257	10573
	% 2,6-*trans*	0	0.8	8.7	15.9	21.9	26.9	31.0	34.5	37.3	39.6
GC area Naphthalene			578.6	579.5	577.8	576.7	575.4	576.0	572.9	570.8	571.9
GC area 2,6-*cis*			893.7	812.1	746.3	690.5	644.6	607.7	576.1	549.5	530.1
GC area 2,6-*trans*			7.0	77.8	141.3	193.5	237.1	273.6	303.3	327.0	347.8
Conc. 2,6-*cis*	(mol/L)		0.0210	0.0190	0.0175	0.0163	0.0152	0.0143	0.0137	0.0131	0.0126
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0018	0.0033	0.0046	0.0056	0.0065	0.0072	0.0078	0.0083
ln [*trans* eq/*trans* eq-*trans* t]			0.0158	0.1907	0.3802	0.5690	0.7612	0.9527	1.1541	1.3504	1.5440
ln [*cis* t-*cis* eq]			-4.54	-4.74	-4.93	-5.12	-5.32	-5.51	-5.70	-5.89	-6.08
cis + *trans*	(mol/L)		0.0211	0.0209	0.0209	0.0208	0.0208	0.0208	0.0208	0.0209	0.0208
1/(*cis* t-*cis* eq)			93.69	114.56	138.14	167.83	203.58	248.37	298.08	360.72	437.36
1/(*trans* eq-*trans* t)			96.75	115.25	139.29	168.24	203.89	246.91	302.01	367.53	446.03

140-1 (1.54 mM Triflic Acid)	time (sec)	11888	13204	15992	18622	23881	29138	39652	89609	2335555
	% 2,6-*trans*	41.5	43.0	45.4	46.9	48.6	49.5	50.1	50.4	50.5
GC area Naphthalene		573.5	570.1	571.7	571.3	574.3	569.1	568.0	570.4	566.1
GC area 2,6-*cis*		515.0	498.4	477.4	463.2	449.8	441.5	433.6	425.8	395.4
GC area 2,6-*trans*		365.3	376.3	396.4	408.7	425.5	431.9	435.6	433.2	402.6
Conc. 2,6-*cis*	(mol/L)	0.0122	0.0119	0.0113	0.0110	0.0106	0.0105	0.0104	0.0101	0.0095
Conc. 2,6-*trans*	(mol/L)	0.0086	0.0090	0.0094	0.0097	0.0101	0.0103	0.0104	0.0103	0.0097
ln [*trans* eq/*trans* eq-*trans* t]		1.7358	1.9215	2.2700	2.5924	3.1739	3.9877	4.8015	4.0268	2.5223
ln [*cis* t-*cis* eq]		-6.27	-6.46	-6.87	-7.25	-8.00	-8.36	-9.63	#NUM!	#NUM!
cis + *trans*	(mol/L)	0.0208	0.0208	0.0208	0.0207	0.0207	0.0208	0.0208	0.0204	0.0191
1/(*cis* t-*cis* eq)		528.03	636.47	962.33	1409.30	2983.06	4266.91	15174.35	-6119.90	-1226.08
1/(*trans* eq-*trans* t)		540.34	650.58	921.87	1272.57	2276.19	5136.16	11589.35	5340.82	1186.38

Table A.1 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.54 mM trifluoromethanesulphonic acid in nitromethane at 30°C

140-2 (1.27 mM Triflic Acid)	time (sec)	0	577	3207	5837	8467	11095	13725	16353	18983	21611
	% 2,6-*trans*	0	2.9	13.3	21.1	26.9	31.4	34.9	37.7	39.9	41.6
GC area Naphthalene			569.3	569.5	569.5	571.2	571.3	570.4	566.7	566.8	565.8
GC area 2,6-*cis*			862.0	759.9	690.1	640.8	600.2	568.9	544.4	525.9	509.5
GC area 2,6-*trans*			25.5	116.6	184.4	236.3	275.0	305.0	328.8	348.6	363.4
Conc. 2,6-*cis*	(mol/L)		0.02056	0.01812	0.01645	0.01523	0.01427	0.01354	0.01304	0.01260	0.01223
Conc. 2,6-*trans*	(mol/L)		0.00061	0.00278	0.00440	0.00562	0.00654	0.00726	0.00788	0.00835	0.00872
ln [*trans* eq/*trans* eq-*trans* t]			0.0597	0.3076	0.5426	0.7657	0.9742	1.1761	1.3876	1.5866	1.7756
ln [*cis* t-*cis* eq]			-4.589	-4.864	-5.107	-5.332	-5.556	-5.763	-5.935	-6.120	-6.305
cis + *trans*	(mol/L)		0.0212	0.0209	0.0209	0.0209	0.0208	0.0208	0.0209	0.0210	0.0209

140-2 (1.27 mM Triflic Acid)	time (sec)	29494	32121	34752	37382	40011	45272	53161	61051	74195
	% 2,6-*trans*	45.2	45.9	46.6	47.1	47.6	48.3	49.0	49.4	49.8
GC area Naphthalene		570.9	570.2	567.8	566.2	571.5	571.9	569.7	569.4	564.0
GC area 2,6-*cis*		478.7	471.0	464.9	461.3	457.2	451.7	442.2	438.1	434.4
GC area 2,6-*trans*		394.3	400.1	405.3	411.1	414.9	421.3	424.1	427.3	430.7
Conc. 2,6-*cis*	(mol/L)	0.01139	0.01122	0.01112	0.01106	0.01086	0.01072	0.01054	0.01045	0.01046
Conc. 2,6-*trans*	(mol/L)	0.00938	0.00953	0.00969	0.00986	0.00986	0.01000	0.01011	0.01019	0.01037
ln [*trans* eq/*trans* eq-*trans* t]		2.2367	2.3799	2.5655	2.7965	2.7947	3.0509	3.2892	3.5231	4.3885
ln [*cis* t-*cis* eq]		-6.922	-7.110	-7.239	-7.318	-7.677	-8.032	-8.874	-9.950	-9.743
cis + *trans*	(mol/L)	0.0208	0.0207	0.0208	0.0209	0.0207	0.0207	0.0206	0.0206	0.0208

Table A.2 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.27 mM trifluoromethanesulphonic acid in nitromethane at 30°C

140-3 (0.76 mM Triflic Acid)	time (sec)	0	57	1371	2684	3999	5313	9260	22410
	% 2,6-*trans*	0	0.4	1.2	2.1	2.9	3.6	5.4	9.2
GC area Naphthalene			572.0	575.1	572.7	572.6	572.8	570.6	570.7
GC area 2,6-*cis*			887.5	879.9	866.7	857.8	849.6	835.1	797.8
GC area 2,6-*trans*			3.40	11.10	18.90	25.80	32.10	48.00	80.50
Conc. 2,6-*cis*	(mol/L)		0.0211	0.0208	0.0205	0.0203	0.0201	0.0199	0.0190
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0003	0.0004	0.0006	0.0008	0.0011	0.0019
ln [*trans* eq/*trans* eq-*trans* t]			0.009	0.030	0.051	0.070	0.088	0.136	0.239
ln [*cis* t-*cis* eq]			-4.417	-4.442	-4.461	-4.479	-4.497	-4.521	-4.607
cis + *trans*	(mol/L)		0.0211	0.0210	0.0210	0.0210	0.0209	0.0210	0.0209

140-3 (0.76 mM Triflic Acid)	time (sec)	35555	48702	61850	108480	174262	288734	1221867	2237083
	% 2,6-*trans*	11.0	12.0	12.6	13.5	14.3	15.0	17.3	18.0
GC area Naphthalene		566.8	560.9	557.3	558.0	554.8	564.8	549.6	554.8
GC area 2,6-*cis*		780.1	766.7	758.6	745.3	736.8	740.1	711.9	705.1
GC area 2,6-*trans*		96.60	104.70	109.40	116.30	122.50	130.60	149.20	155.20
Conc. 2,6-*cis*	(mol/L)	0.0187	0.0186	0.0185	0.0181	0.0180	0.0178	0.0176	0.0173
Conc. 2,6-*trans*	(mol/L)	0.0023	0.0025	0.0027	0.0028	0.0030	0.0031	0.0037	0.0038
ln [*trans* eq/*trans* eq-*trans* t]		0.297	0.331	0.351	0.378	0.405	0.429	0.527	0.548
ln [*cis* t-*cis* eq]		-4.637	-4.650	-4.658	-4.695	-4.707	-4.734	-4.757	-4.797
cis + *trans*	(mol/L)	0.0210	0.0211	0.0211	0.0210	0.0210	0.0209	0.0213	0.0211

Table A.3 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM trifluoromethanesulphonic acid in nitromethane at 30°C

140-4 (1.0 mM Triflic Acid)	time (sec)	0	85	1398	2716	4033	5349	6665	7980	9296	10611
	% 2,6-*trans*	0	0.4	3.6	6.6	9.2	11.5	13.3	15.6	17.3	18.9
GC area Naphthalene			570.9	567.6	567.3	575.2	570.3	562.9	571.7	571.8	556.0
GC area 2,6-*cis*			889.0	851.0	827.6	805.4	781.6	753.4	744.5	732.7	690.9
GC area 2,6-*trans*			4.0	32.1	58.6	81.7	102.0	116.0	137.4	153.1	160.8
Conc. 2,6-*cis*	(mol/L)		0.0211	0.0204	0.0198	0.0190	0.0186	0.0182	0.0177	0.0174	0.0169
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0008	0.0014	0.0019	0.0024	0.0028	0.0033	0.0036	0.0039
ln [*trans* eq/*trans* eq-*trans* t]			0.0140	0.0815	0.1497	0.2099	0.2707	0.3182	0.3814	0.4350	0.4790
ln [*cis* t-*cis* eq]			-4.529	-4.604	-4.661	-4.749	-4.796	-4.851	-4.915	-4.955	-5.032
cis + *trans*	(mol/L)		0.0212	0.0211	0.0212	0.0209	0.0210	0.0210	0.0209	0.0210	0.0208

140-4 (1.0 mM Triflic Acid)	time (sec)	18504	23765	31654	40858	47437	60709	73750	127685	193504
	% 2,6-*trans*	25.9	28.9	31.9	34.0	35.1	36.3	37.0	38.1	38.4
GC area Naphthalene		571.8	569.4	565.5	564.1	563.4	560.4	559.8	555.6	546.2
GC area 2,6-*cis*		653.9	625.0	596.3	577.2	565.1	554.1	546.1	531.7	526.0
GC area 2,6-*trans*		228.7	253.6	279.3	297.6	305.1	316.0	321.4	327.0	327.7
Conc. 2,6-*cis*	(mol/L)	0.0155	0.0149	0.0143	0.0139	0.0136	0.0134	0.0132	0.0130	0.0131
Conc. 2,6-*trans*	(mol/L)	0.0054	0.0060	0.0067	0.0072	0.0074	0.0077	0.0078	0.0080	0.0081
ln [*trans* eq/*trans* eq-*trans* t]		0.7434	0.8759	1.0401	1.1722	1.2326	1.3375	1.3896	1.4678	1.5343
ln [*cis* t-*cis* eq]		-5.263	-5.392	-5.529	-5.642	-5.723	-5.784	-5.844	-5.935	-5.905
cis + *trans*	(mol/L)	0.0210	0.0210	0.0210	0.0211	0.0210	0.0211	0.0210	0.0210	0.0212

Table A.4 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.0 mM trifluoromethanesulphonic acid in nitromethane at 30°C

140-5 (1.76 mM Triflic Acid)	time (sec)	0	20	1312	2628	3943	5259	6574	7891	9207	10523
	% 2,6-*trans*	0	0.9	9.0	16.0	22.0	27.0	31.2	34.7	37.6	39.9
GC area Naphthalene			571.1	578.7	577.5	575.7	577.3	577.6	574.9	571.3	572.3
GC area 2,6-*cis*			888.9	808.1	743.1	691.5	644.7	607.0	574.9	548.5	526.0
GC area 2,6-*trans*			8.1	79.5	141.7	194.9	238.8	275.2	306.1	329.9	349.1
Conc. 2,6-*cis*	(mol/L)		0.0211	0.0190	0.0175	0.0163	0.0152	0.0143	0.0136	0.0130	0.0125
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0019	0.0033	0.0046	0.0056	0.0065	0.0072	0.0078	0.0083
ln [*trans* eq/*trans* eq-*trans* t]			0.0187	0.1977	0.3862	0.5834	0.7767	0.9731	1.1881	1.4023	1.5918
ln [*cis* t-*cis* eq]			-4.525	-4.749	-4.937	-5.114	-5.326	-5.529	-5.720	-5.901	-6.128
cis + *trans*	(mol/L)		0.0213	0.0208	0.0208	0.0209	0.0208	0.0207	0.0208	0.0209	0.0208

140-5 (1.76 mM Triflic Acid)	time (sec)	15788	17106	18423	19741	21059	22377	25013	27649	31605
	% 2,6-*trans*	45.6	46.4	47.1	47.6	48.1	48.5	49.0	49.4	49.8
GC area Naphthalene		574.3	573.5	573.2	574.1	566.3	564.1	567.6	570.3	567.5
GC area 2,6-*cis*		476.1	468.1	462.1	457.9	453.4	449.2	442.1	438.9	434.5
GC area 2,6-*trans*		398.7	405.0	410.8	416.2	419.9	422.4	425.2	428.2	430.8
Conc. 2,6-*cis*	(mol/L)	0.0113	0.0111	0.0109	0.0108	0.0109	0.0108	0.0106	0.0105	0.0104
Conc. 2,6-*trans*	(mol/L)	0.0094	0.0096	0.0097	0.0098	0.0101	0.0102	0.0102	0.0102	0.0103
ln [*trans* eq/*trans* eq-*trans* t]		2.3692	2.5517	2.7449	2.9292	3.4460	3.8027	3.8213	3.9291	4.7282
ln [*cis* t-*cis* eq]		-6.952	-7.152	-7.343	-7.542	-7.467	-7.575	-8.193	-8.803	-9.245
cis + *trans*	(mol/L)	0.0207	0.0207	0.0207	0.0207	0.0209	0.0210	0.0207	0.0206	0.0207

Table A.5 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.76 mM trifluoromethanesulphonic acid in nitromethane at 30°C

141-1 (2.5 mM Triflic Acid)	time (sec)	0	1368	3996	6626	9257	11888	14519	43501.00
	% 2,6-*trans*	0	16.9	34.8	43.5	47.4	49.1	49.9	50.5
GC area Naphthalene			564.2	567.2	565.4	564.7	568.1	566.8	561.6
GC area 2,6-*cis*			734.8	573.0	494.8	457.7	443.0	434.3	418.8
GC area 2,6-*trans*			149.6	305.6	380.2	413.0	427.5	432.5	426.6
Conc. 2,6-*cis*	(mol/L)		0.0177	0.0137	0.0119	0.0110	0.0106	0.0104	0.0101
Conc. 2,6-*trans*	(mol/L)		0.0036	0.0073	0.0091	0.0099	0.0102	0.0104	0.0103
ln [*trans* eq/*trans* eq-*trans* t]			0.4199	1.1933	2.0374	2.9155	3.6182	4.3282	4.0376
ln [*cis* t-*cis* eq]			-4.9220	-5.7085	-6.5134	-7.4086	-8.5750	-12.2858	#NUM!
cis + *trans*	(mol/L)		0.0213	0.0210	0.0210	0.0209	0.0208	0.0208	0.0204
		7/28/03 11:32am							
141-2 (3.8 mM Triflic Acid)	time (sec)	0	57	2682	5312	7942	10574	13204	44818.00
	% 2,6-*trans*	0	3.2	39.8	48.2	50.0	50.4	50.4	50.5
GC area Naphthalene			569.1	577.4	572.3	574.8	571.7	576.9	571.8
GC area 2,6-*cis*			867.1	538.4	458.4	442.3	434.4	433.2	414.4
GC area 2,6-*trans*			28.6	356.4	427.3	442.5	440.9	440.3	422.0
Conc. 2,6-*cis*	(mol/L)		0.0207	0.0127	0.0109	0.0104	0.0103	0.0102	0.0098
Conc. 2,6-*trans*	(mol/L)		0.0007	0.0084	0.0101	0.0105	0.0105	0.0104	0.0100
ln [*trans* eq/*trans* eq-*trans* t]			0.0679	1.6007	3.3690	5.4201	5.9342	4.3442	3.0886
ln [*cis* t-*cis* eq]			-4.5670	-6.0483	-7.4586	-8.8129	-10.9355	#NUM!	#NUM!
cis + *trans*	(mol/L)		0.0214	0.0210	0.0210	0.0209	0.0208	0.0206	0.0199

Table A.6 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 2.5 mM trifluoromethanesulphonic acid in nitromethane at 30°C

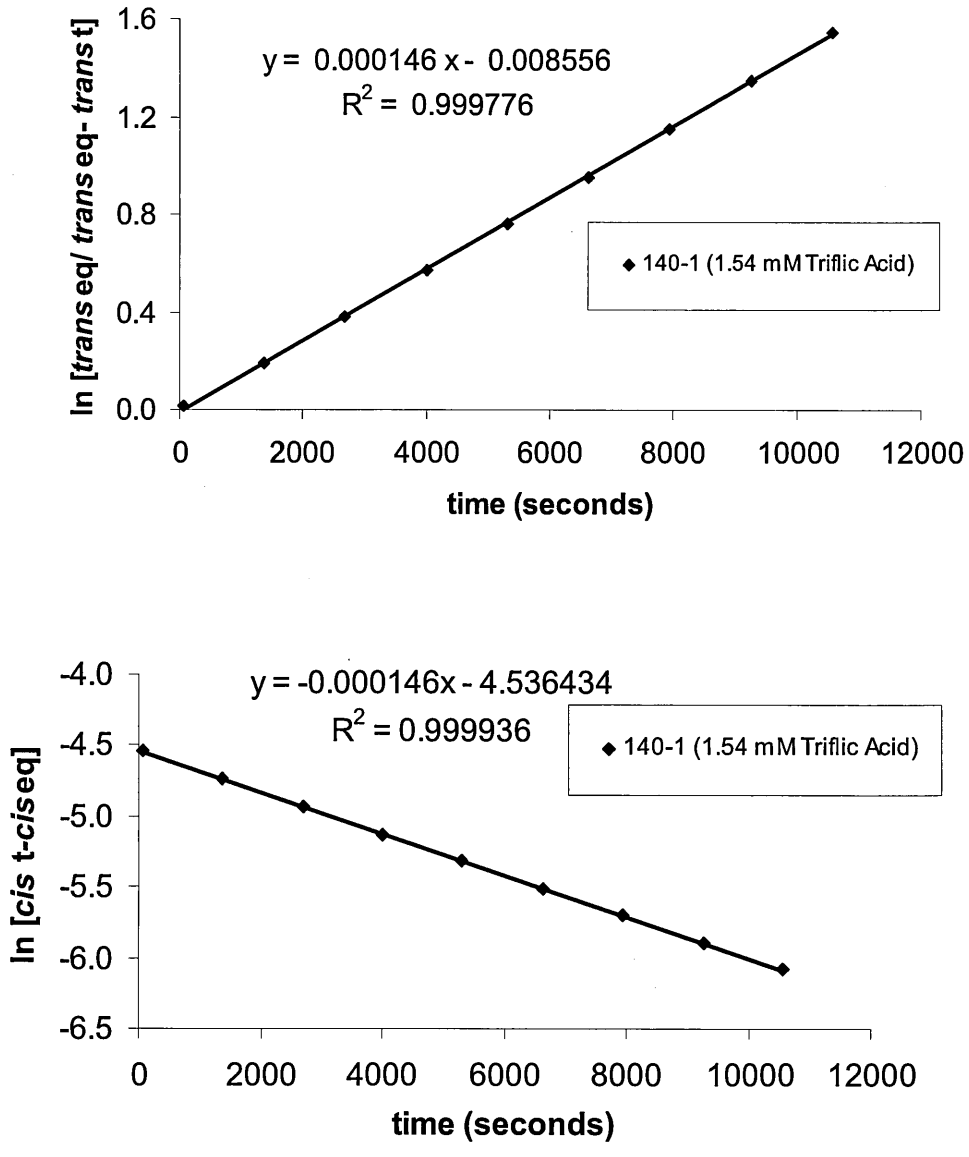


Figure A.1 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.54 mM trifluoromethanesulphonic acid in nitromethane at 30°C

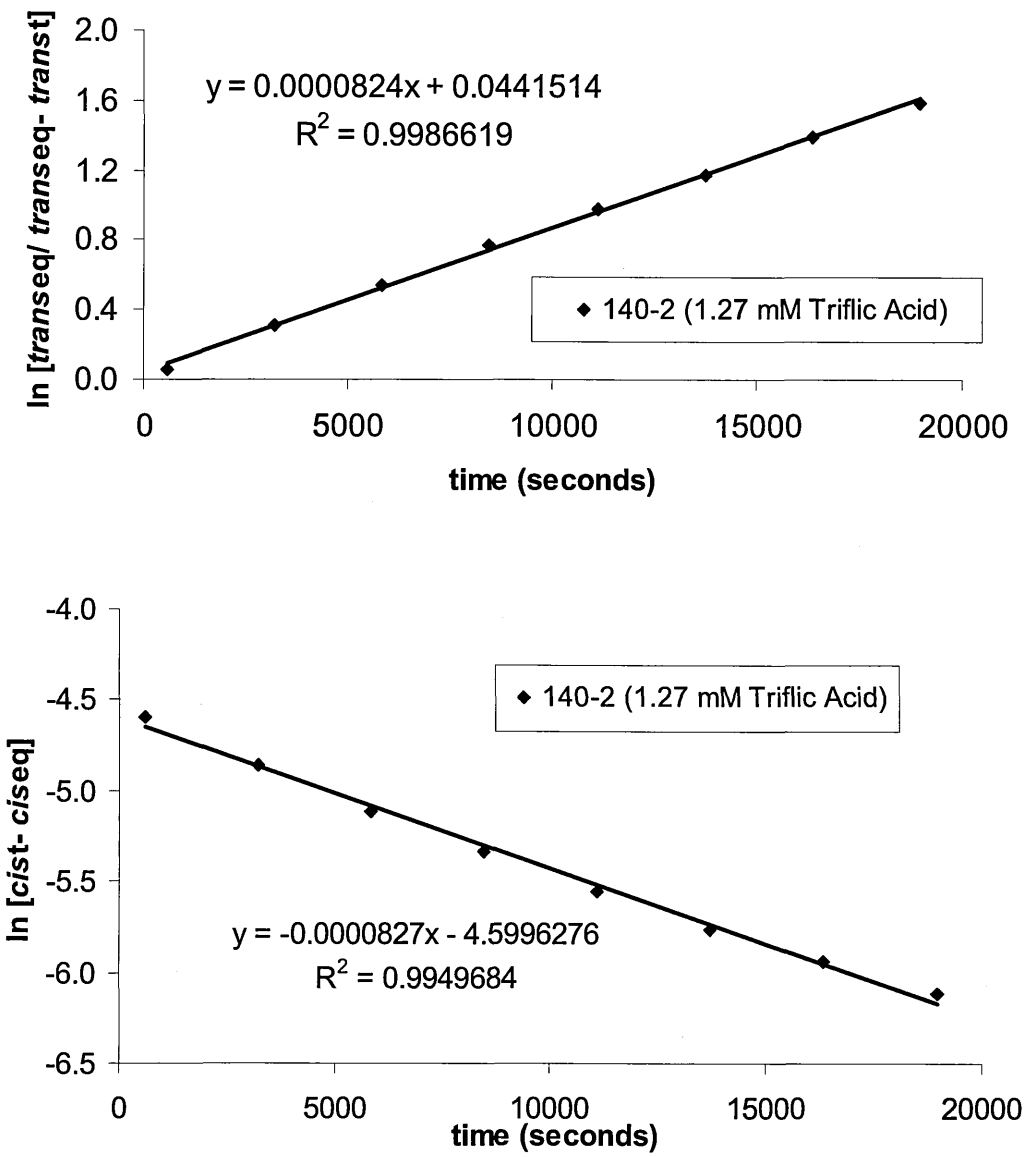
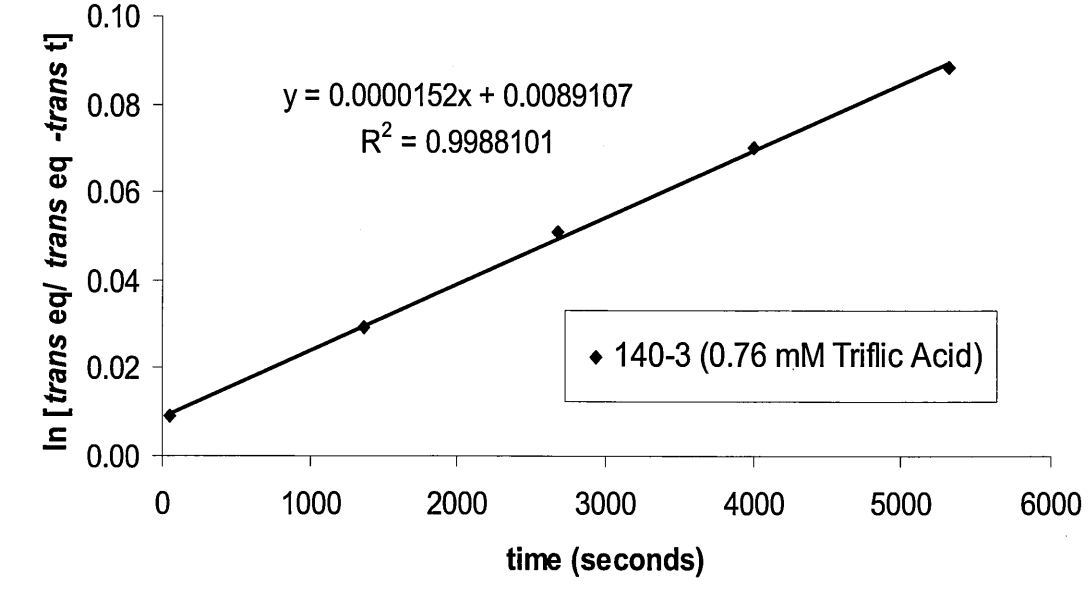


Figure A.2 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.27 mM trifluoromethanesulphonic acid in nitromethane at 30°C



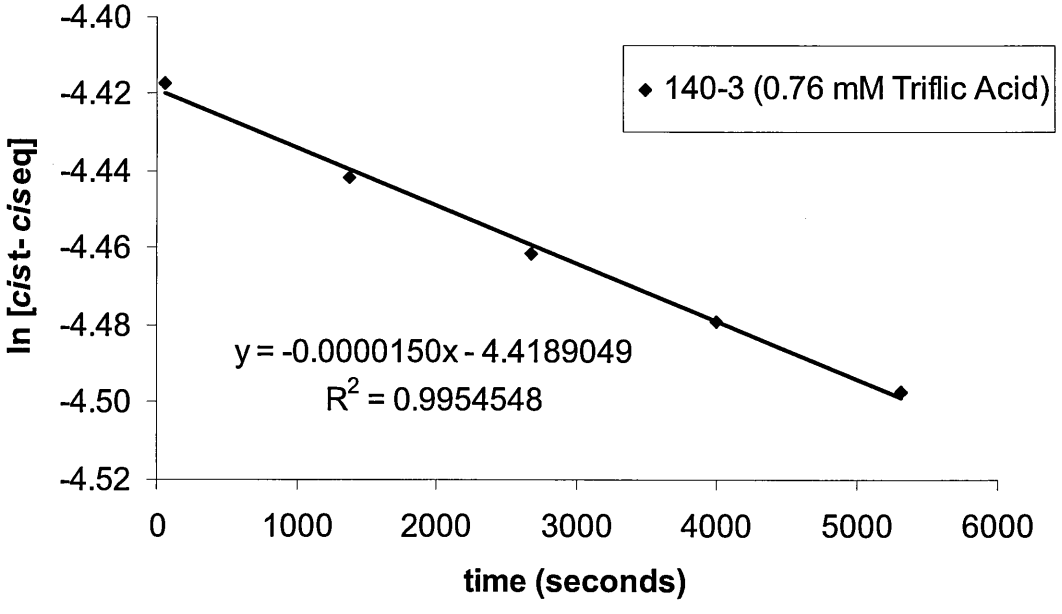


Figure A.3 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM trifluoromethanesulphonic acid in nitromethane at 30°C

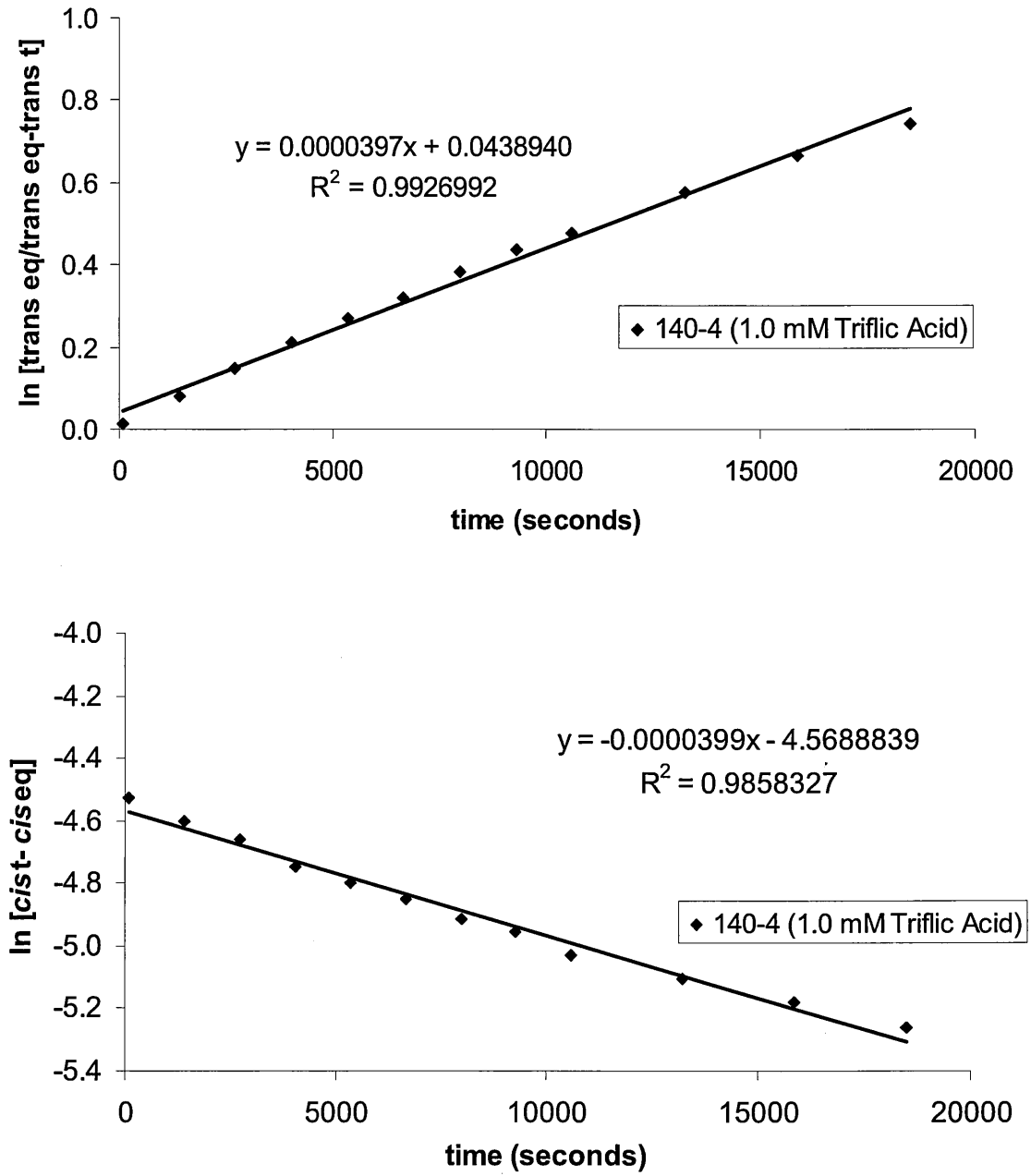


Figure A.4 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.0 mM trifluoromethanesulphonic acid in nitromethane at 30°C

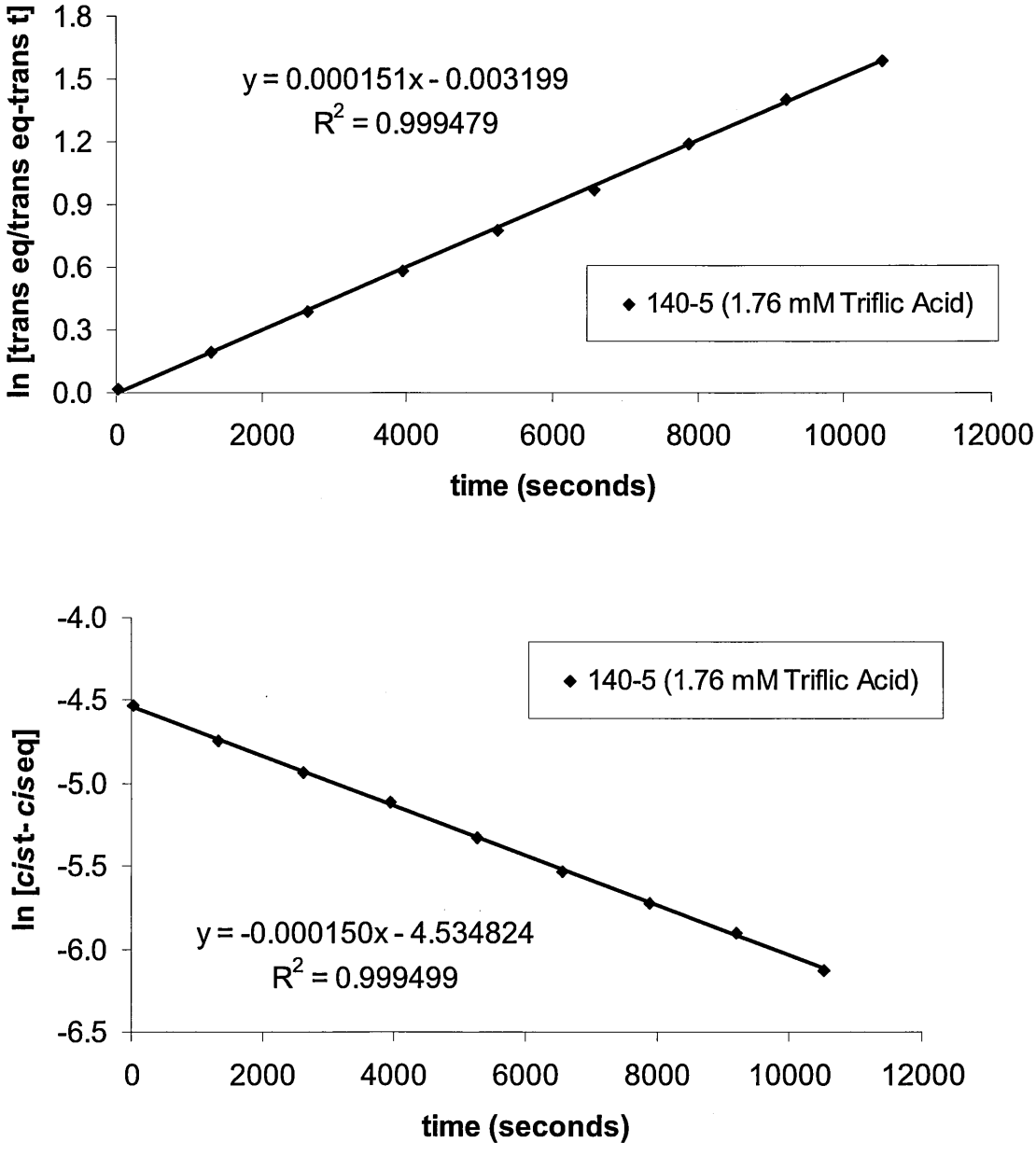


Figure A.5 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.8 mM trifluoromethanesulphonic acid in nitromethane at 30°C

148-3 (0.81mM Triflic Acid)	time (sec)	0	45	2674	5304	7936	10565	13198	15831	18466
	% 2,6-*trans*	0	0.5	4.8	8.4	11.6	14.5	17.2	19.6	21.8
area Naphthalene			679.6	681.7	682.4	684.5	680.9	682.8	682.4	681.6
area 2,6-*cis*			927.4	885.6	858.5	829.1	797.1	775.0	751.6	736.7
area 2,6-*trans*			5.1	44.6	78.3	108.5	135.1	160.9	183.6	205.8
Conc. 2,6-*cis*	(mol/L)		0.0185	0.0176	0.0171	0.0164	0.0159	0.0154	0.0150	0.0147
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0009	0.0016	0.0022	0.0027	0.0032	0.0037	0.0041
ln [*trans* eq/*trans* eq-*trans* t]			0.0109	0.0993	0.1812	0.2600	0.3377	0.4161	0.4921	0.5730
ln [*cis* t -*cis* eq]			-4.685	-4.787	-4.856	-4.941	-5.021	-5.097	-5.175	-5.226
cis + *trans*	(mol/L)		0.0186	0.0185	0.0186	0.0186	0.0186	0.0186	0.0186	0.0188

148-3 (0.81mM Triflic Acid)	time (sec)	39542	42177	44811	47445	52710	57971	63237	68501
	% 2,6-*trans*	33.6	34.6	35.4	36.2	37.6	38.8	39.7	40.6
area Naphthalene		680.4	679.8	677.5	679.2	676.7	679.7	678.6	679.3
area 2,6-*cis*		620.4	614.4	606.4	595.7	582.2	572.3	561.9	552.9
area 2,6-*trans*		314.2	324.6	333.0	338.2	350.9	362.5	370.5	377.8
Conc. 2,6-*cis*	(mol/L)	0.0124	0.0123	0.0122	0.0119	0.0117	0.0114	0.0112	0.0111
Conc. 2,6-*trans*	(mol/L)	0.0063	0.0065	0.0067	0.0068	0.0070	0.0072	0.0074	0.0076
ln [*trans* eq/*trans* eq-*trans* t]		1.0999	1.1704	1.2380	1.2705	1.3826	1.4715	1.5545	1.6266
ln [*cis* t -*cis* eq]		-5.782	-5.818	-5.859	-5.949	-6.040	-6.150	-6.243	-6.347
cis + *trans*	(mol/L)	0.0187	0.0188	0.0188	0.0187	0.0187	0.0187	0.0187	0.0186

Table A.7 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.81 mM trifluoromethanesulphonic acid in nitromethane at 40°C

149-1 (0.99mM Triflic Acid)	time (sec)	0	41	1354	2669	3984	5297	6611	7925	9238
	% 2,6-*trans*	0	0.8	6.1	10.7	14.7	18.2	21.4	24.1	26.6
area Naphthalene			692.7	695.1	688.2	694.9	674.5	682.4	690.4	686.9
area 2,6-*cis*			936.1	893.4	843.1	813.8	771.2	744.9	718.1	691.9
area 2,6-*trans*			7.8	58.5	101.2	140.2	171.8	202.3	228.2	250.5
Conc. 2,6-*cis*	(mol/L)		0.0184	0.0175	0.0166	0.0159	0.0155	0.0148	0.0141	0.0137
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0011	0.0020	0.0027	0.0035	0.0040	0.0045	0.0050
ln [*trans* eq/*trans* eq-*trans* t]			0.0164	0.1296	0.2388	0.3445	0.4588	0.5590	0.6491	0.7483
ln [*cis* t -*cis* eq]			-4.705	-4.809	-4.915	-5.020	-5.079	-5.199	-5.334	-5.431
cis + *trans*	(mol/L)		0.0185	0.0186	0.0186	0.0186	0.0190	0.0188	0.0186	0.0186

149-1 (0.99mM Triflic Acid)	time (sec)	15810	17124	18439	23789	29047	34307	39573	47475
	% 2,6-*trans*	35.5	36.8	37.9	41.5	44.0	45.7	46.9	48.1
area Naphthalene		683.2	688.7	669.8	677.5	692.0	673.3	685.7	686.4
area 2,6-*cis*		602.1	591.2	579.6	544.7	528.9	506.3	498.5	484.9
area 2,6-*trans*		331.9	344.0	354.0	386.8	415.1	425.7	439.9	448.5
Conc. 2,6-*cis*	(mol/L)	0.0120	0.0117	0.0118	0.0109	0.0104	0.0102	0.0099	0.0096
Conc. 2,6-*trans*	(mol/L)	0.0066	0.0068	0.0072	0.0078	0.0081	0.0086	0.0087	0.0089
ln [*trans* eq/*trans* eq-*trans* t]		1.2099	1.2785	1.4417	1.7415	2.0139	2.4458	2.6137	2.8805
ln [*cis* t -*cis* eq]		-5.927	-6.051	-6.012	-6.427	-6.832	-7.001	-7.467	-8.136
cis + *trans*	(mol/L)	0.0186	0.0184	0.0189	0.0187	0.0185	0.0188	0.0186	0.0185

Table A.8 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.99 mM trifluoromethanesulphonic acid in nitromethane at 40°C

149-2 (0.91mM Triflic Acid)	time (sec)	0	48	1361	2675	5304	7932	10561	13192	15824
	% 2,6-*trans*	0	0.6	3.7	6.5	11.3	15.5	19.1	22.4	25.3
area Naphthalene			685.3	678.1	680.3	692.9	685.8	688.8	693.4	685.5
area 2,6-*cis*			936.0	903.8	881.4	841.9	805.9	763.6	736.2	710.6
area 2,6-*trans*			5.6	35.1	61.0	107.1	147.3	180.4	212.2	240.1
Conc. 2,6-*cis*	(mol/L)		0.0185	0.0181	0.0176	0.0165	0.0160	0.0151	0.0144	0.0141
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0007	0.0012	0.0021	0.0029	0.0036	0.0042	0.0048
ln [*trans* eq/*trans* eq-*trans* t]			0.0119	0.0777	0.1387	0.2527	0.3715	0.4754	0.5835	0.7052
ln [*cis* t -*cis* eq]			-4.684	-4.733	-4.792	-4.934	-5.012	-5.158	-5.275	-5.344
cis + *trans*	(mol/L)		0.0187	0.0188	0.0188	0.0186	0.0189	0.0186	0.0186	0.0188

149-2 (0.91mM Triflic Acid)	time (sec)	26358	28993	31629	34264	36899	39535	42170	47442
	% 2,6-*trans*	33.7	35.2	36.6	37.8	38.9	39.9	40.7	42.1
area Naphthalene		694.6	700.7	679.0	699.4	698.5	693.3	693.7	702.7
area 2,6-*cis*		631.4	620.8	599.5	597.1	585.3	575.3	567.0	558.0
area 2,6-*trans*		321.0	337.6	346.6	362.6	372.5	381.2	389.3	406.0
Conc. 2,6-*cis*	(mol/L)	0.0123	0.0120	0.0120	0.0116	0.0114	0.0113	0.0111	0.0108
Conc. 2,6-*trans*	(mol/L)	0.0063	0.0065	0.0069	0.0070	0.0072	0.0075	0.0076	0.0078
ln [*trans* eq/*trans* eq-*trans* t]		1.1014	1.1907	1.3371	1.3820	1.4713	1.5812	1.6643	1.7996
ln [*cis* t -*cis* eq]		-5.795	-5.903	-5.919	-6.078	-6.176	-6.231	-6.321	-6.514
cis + *trans*	(mol/L)	0.0186	0.0186	0.0189	0.0186	0.0186	0.0187	0.0187	0.0186

Table A.9 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.91 mM trifluoromethanesulphonic acid in nitromethane at 40°C

149-3 (1.3mM Triflic Acid)	time (sec)	0	132	1444	2758	4073	5388	6702	8017
	% 2,6-*trans*	0	0.9	12.3	20.9	27.6	32.7	36.6	39.7
area Naphthalene			685.2	691.9	693.4	691.0	682.7	679.7	687.2
area 2,6-*cis*			926.0	835.7	753.7	684.2	638.8	594.1	572.1
area 2,6-*trans*			8.3	117.0	199.7	260.6	310.0	343.6	376.5
Conc. 2,6-*cis*	(mol/L)		0.0184	0.0164	0.0148	0.0134	0.0127	0.0119	0.0113
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0023	0.0039	0.0051	0.0062	0.0069	0.0074
ln [*trans* eq/*trans* eq-*trans* t]			0.0176	0.2784	0.5342	0.7807	1.0569	1.2961	1.5477
ln [*cis* t -*cis* eq]			-4.710	-4.955	-5.220	-5.498	-5.697	-5.984	-6.238
cis + *trans*	(mol/L)		0.0185	0.0187	0.0187	0.0186	0.0189	0.0187	0.0187

149-3 (1.3mM Triflic Acid)	time (sec)	9331	10647	11962	13278	15907	18534	66225
	% 2,6-*trans*	42.0	43.8	45.2	46.3	47.8	48.7	50.4
area Naphthalene		683.9	685.8	682.6	682.0	682.0	681.4	687.8
area 2,6-*cis*		549.4	529.7	517.5	503.2	489.8	477.0	461.1
area 2,6-*trans*		398.3	413.4	426.8	434.0	448.7	452.5	468.5
Conc. 2,6-*cis*	(mol/L)	0.0109	0.0105	0.0103	0.0100	0.0098	0.0095	0.0091
Conc. 2,6-*trans*	(mol/L)	0.0079	0.0082	0.0085	0.0086	0.0089	0.0090	0.0092
ln [*trans* eq/*trans* eq-*trans* t]		1.8131	2.0112	2.2872	2.4582	2.9073	3.0840	3.8525
ln [*cis* t -*cis* eq]		-6.464	-6.778	-6.965	-7.310	-7.819	-8.768	#NUM!
cis + *trans*	(mol/L)	0.0188	0.0187	0.0188	0.0187	0.0187	0.0185	0.0184

Table A.10 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.3 mM trifluoromethanesulphonic acid in nitromethane at 40°C

150-1 (1.1mM Triflic Acid)	time (sec)	0	52	1367	2682	3998	5314	6630	7947	9264
	% 2,6-*trans*	0	0.7	7.2	12.7	17.4	21.5	25.0	28.1	30.8
area Naphthalene			688.2	692.0	694.5	694.0	695.3	690.5	687.6	699.3
area 2,6-*cis*			946.8	890.7	838.8	795.6	760.1	722.9	687.7	664.0
area 2,6-*trans*			6.3	69.3	122.5	167.9	207.9	241.2	268.9	295.6
Conc. 2,6-*cis*	(mol/L)		0.0187	0.0175	0.0164	0.0156	0.0148	0.0142	0.0136	0.0129
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0014	0.0024	0.0033	0.0041	0.0047	0.0053	0.0057
ln [*trans* eq/*trans* eq-*trans* t]			0.0133	0.1563	0.2941	0.4300	0.5655	0.7024	0.8322	0.9432
ln [*cis* t -*cis* eq]			-4.680	-4.819	-4.962	-5.089	-5.213	-5.336	-5.477	-5.657
cis + *trans*	(mol/L)		0.0188	0.0188	0.0188	0.0189	0.0189	0.0190	0.0189	0.0186

150-1 (1.1mM Triflic Acid)	time (sec)	13215	14530	15846	17162	19795	22428	26378	34276
	% 2,6-*trans*	36.9	38.5	39.8	41.0	42.9	44.3	45.9	47.8
area Naphthalene		692.3	694.5	693.6	701.1	693.2	690.9	693.6	688.0
area 2,6-*cis*		607.2	592.2	578.2	563.9	548.4	532.0	517.4	495.6
area 2,6-*trans*		355.7	370.1	382.0	391.1	411.7	423.9	439.8	454.7
Conc. 2,6-*cis*	(mol/L)	0.0119	0.0116	0.0113	0.0109	0.0107	0.0105	0.0101	0.0098
Conc. 2,6-*trans*	(mol/L)	0.0070	0.0072	0.0075	0.0076	0.0081	0.0083	0.0086	0.0090
ln [*trans* eq/*trans* eq-*trans* t]		1.3556	1.4689	1.5877	1.6390	1.9516	2.1743	2.4767	3.0948
ln [*cis* t -*cis* eq]		-5.988	-6.129	-6.256	-6.488	-6.613	-6.853	-7.223	-7.871
cis + *trans*	(mol/L)	0.0189	0.0188	0.0188	0.0185	0.0188	0.0188	0.0187	0.0188

Table A.11 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.1 mM trifluoromethanesulphonic acid in nitromethane at 40°C

150-2 (1.3mM Triflic Acid)	time (sec)	0	143	1456	2771	4085	5400	6714	8028	9340
	% 2,6-*trans*	0	0.9	11.4	19.6	25.9	30.9	34.8	37.9	40.4
area Naphthalene			685.9	701.2	703.1	700.9	692.7	689.6	694.5	692.0
area 2,6-*cis*			937.4	847.9	774.5	711.6	658.3	621.8	595.4	570.8
area 2,6-*trans*			8.7	109.2	188.3	248.6	294.2	332.3	363.7	386.6
Conc. 2,6-*cis*	(mol/L)		0.0186	0.0164	0.0150	0.0138	0.0129	0.0122	0.0116	0.0112
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0021	0.0036	0.0048	0.0058	0.0065	0.0071	0.0076
ln [*trans* eq/*trans* eq-*trans* t]			0.0185	0.2548	0.4892	0.7182	0.9507	1.1911	1.4126	1.6453
ln [*cis* t-*cis* eq]			-4.682	-4.945	-5.175	-5.407	-5.626	-5.828	-6.057	-6.266
cis + *trans*	(mol/L)		0.0187	0.0185	0.0186	0.0186	0.0187	0.0188	0.0188	0.0188

150-2 (1.3mM Triflic Acid)	time (sec)	10654	11968	13283	14597	15911	17225	19854	21168
	% 2,6-*trans*	42.3	43.9	45.1	46.1	46.9	47.5	48.5	48.8
area Naphthalene		698.4	700.3	693.8	690.3	689.6	694.9	696.8	697.5
area 2,6-*cis*		550.3	535.2	522.3	510.5	502.2	498.8	487.0	482.9
area 2,6-*trans*		403.9	418.8	429.9	436.9	443.7	452.1	458.0	460.3
Conc. 2,6-*cis*	(mol/L)	0.0107	0.0104	0.0102	0.0100	0.0099	0.0097	0.0095	0.0094
Conc. 2,6-*trans*	(mol/L)	0.0079	0.0081	0.0084	0.0086	0.0087	0.0088	0.0089	0.0090
ln [*trans* eq/*trans* eq-*trans* t]		1.8044	1.9943	2.2547	2.4567	2.6516	2.8106	2.9858	3.0643
ln [*cis* t-*cis* eq]		-6.572	-6.833	-6.989	-7.206	-7.437	-7.713	-8.566	-9.199
cis + *trans*	(mol/L)	0.0186	0.0185	0.0186	0.0186	0.0186	0.0186	0.0184	0.0184

Table A.12 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.3 mM trifluoromethanesulphonic acid in nitromethane at 40°C

150-3 (1.4mM Triflic Acid)	time (sec)	0	154	1467	2781	4096	5412	6728	8043	9357
	% 2,6-*trans*	0	0.9	13.0	22.0	28.8	33.9	37.7	40.6	42.9
area Naphthalene			699.4	713.5	713.5	716.4	710.5	708.0	701.6	708.4
area 2,6-*cis*			955.9	849.2	758.2	697.3	642.9	603.4	572.8	550.3
area 2,6-*trans*			9.0	126.7	213.7	281.4	329.0	365.4	392.3	413.4
Conc. 2,6-*cis*	(mol/L)		0.01856	0.01616	0.01443	0.01322	0.01229	0.01157	0.01109	0.01055
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0024	0.0041	0.0053	0.0063	0.0070	0.0076	0.0079
ln [*trans* eq/*trans* eq-*trans* t]			0.0188	0.2964	0.5668	0.8380	1.1054	1.3686	1.6489	1.8515
ln [*cis* t -*cis* eq]			-4.671	-4.967	-5.253	-5.517	-5.781	-6.044	-6.273	-6.609
cis + *trans*	(mol/L)		0.0187	0.0186	0.0185	0.0186	0.0186	0.0186	0.0187	0.0185

150-3 (1.4mM Triflic Acid)	time (sec)	10673	11989	13305	14621	17252	19882	23827
	% 2,6-*trans*	44.6	45.9	46.9	47.7	48.7	49.3	50.4
area Naphthalene		707.5	695.5	700.4	710.7	708.9	701.4	694.8
area 2,6-*cis*		533.2	518.2	510.3	505.0	493.8	488.2	468.7
area 2,6-*trans*		429.2	439.6	450.5	459.8	468.9	475.2	476.0
Conc. 2,6-*cis*	(mol/L)	0.01023	0.01012	0.00989	0.00965	0.00946	0.00945	0.00916
Conc. 2,6-*trans*	(mol/L)	0.0082	0.0086	0.0087	0.0088	0.0090	0.0092	0.0093
ln [*trans* eq/*trans* eq-*trans* t]		2.0902	2.4425	2.6472	2.7271	3.1124	3.8490	4.5716
ln [*cis* t -*cis* eq]		-6.875	-6.994	-7.274	-7.709	-8.260	-8.288	#NUM!
cis + *trans*	(mol/L)	0.0185	0.0187	0.0186	0.0184	0.0184	0.0187	0.0185

Table A.13 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.4 mM trifluoromethanesulphonic acid in nitromethane at 40°C

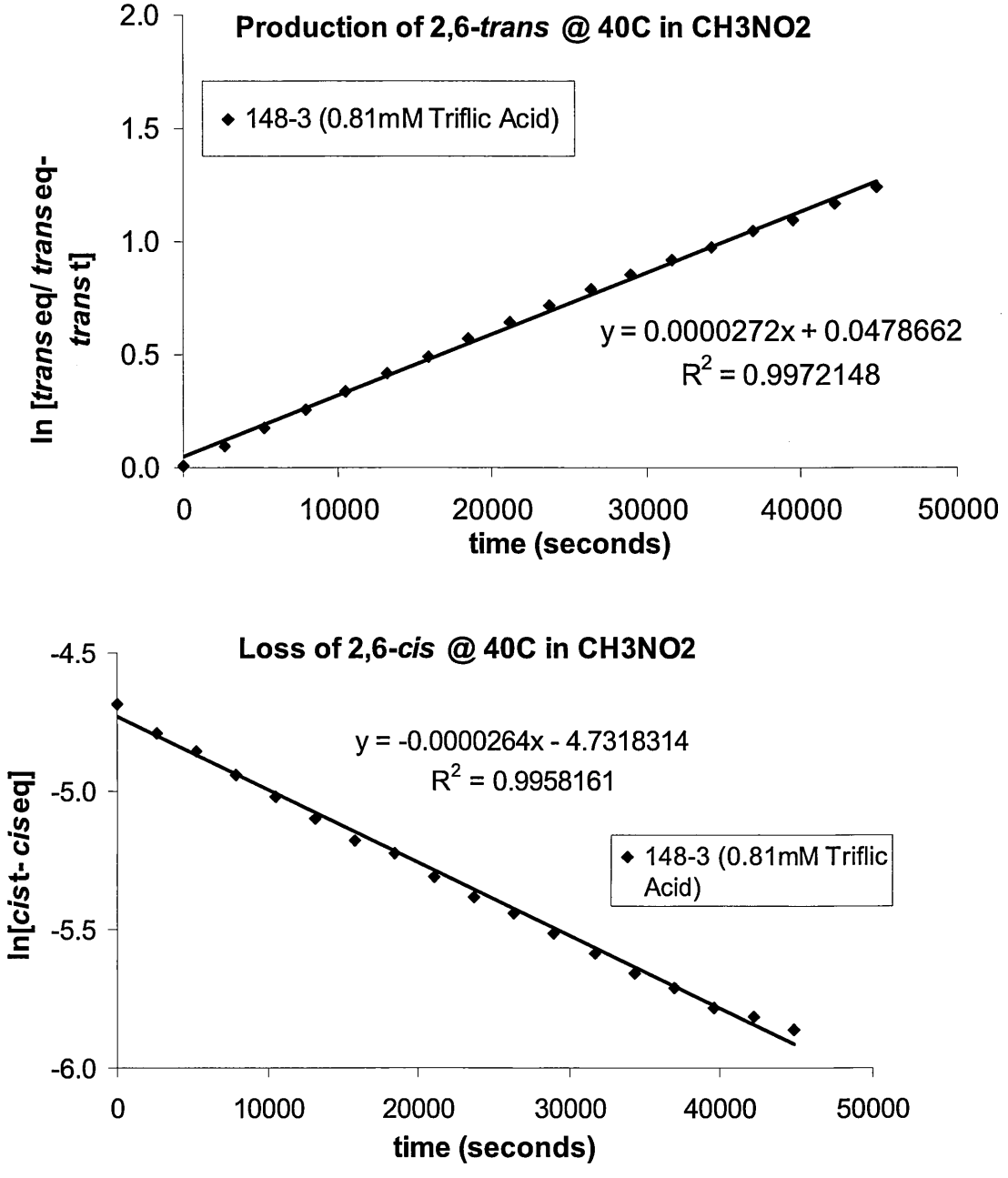


Figure A.6 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.81 mM trifluoromethanesulphonic acid in nitromethane at 40°C

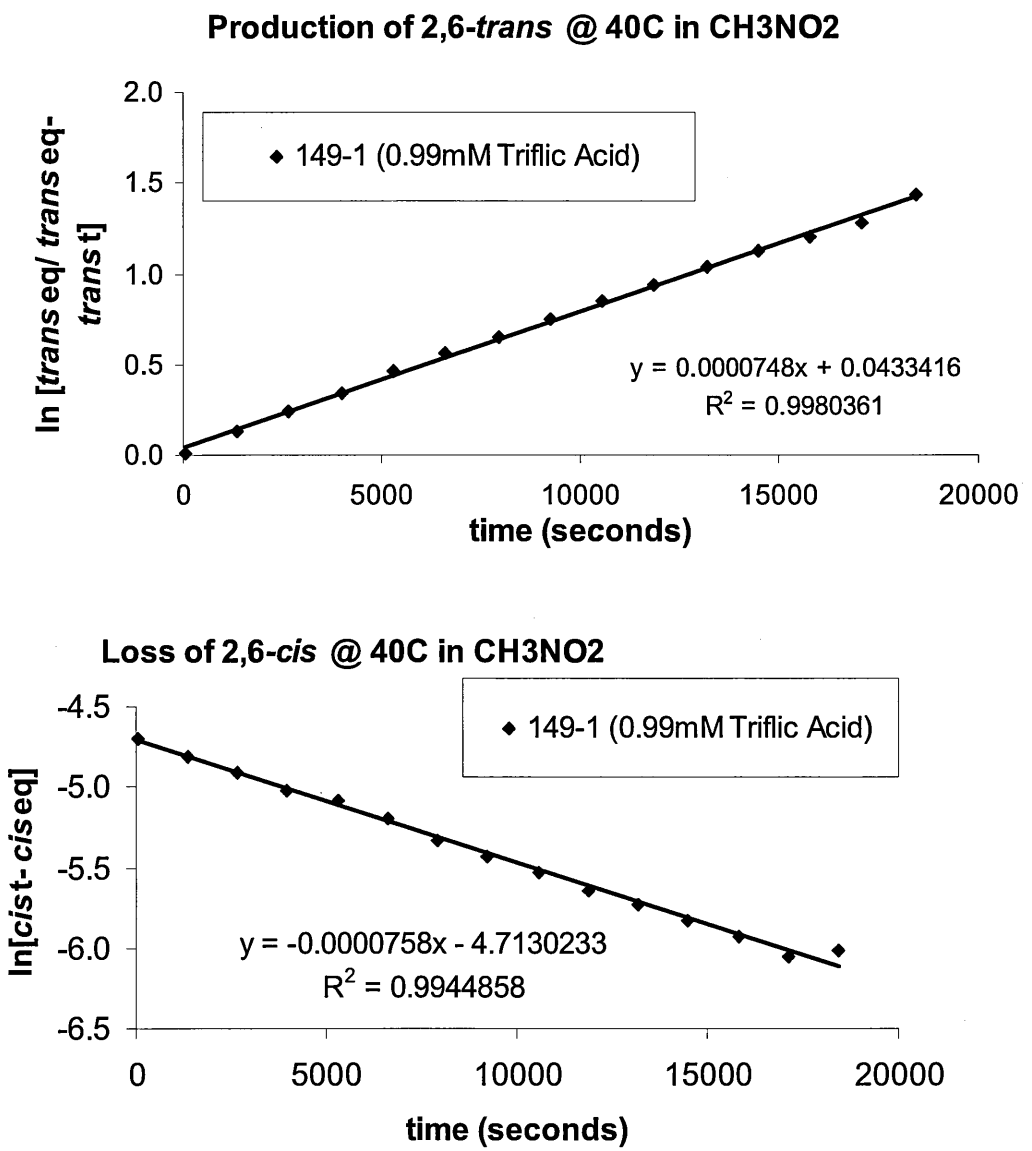


Figure A.7 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.0 mM trifluoromethanesulphonic acid in nitromethane at 40°C

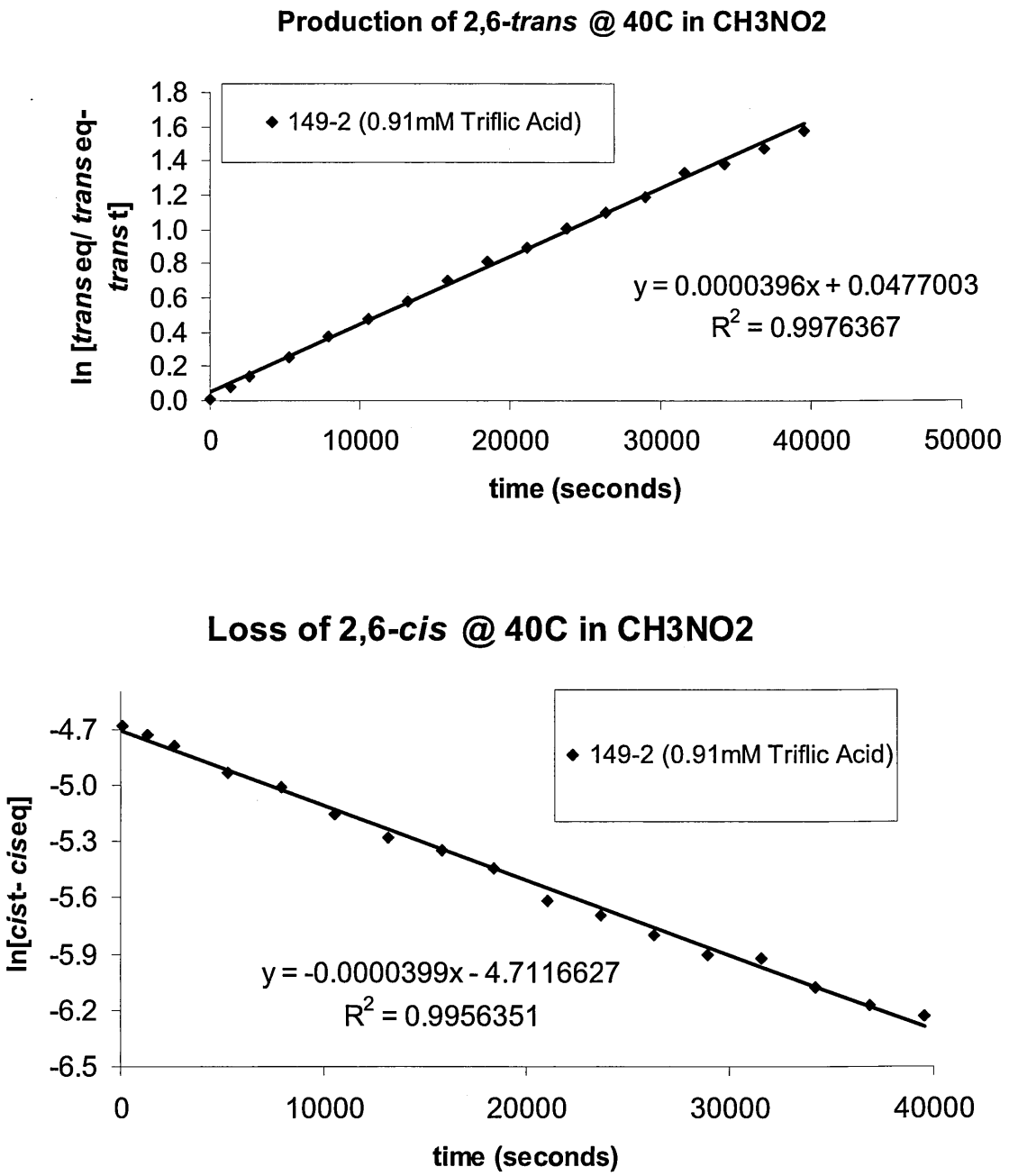
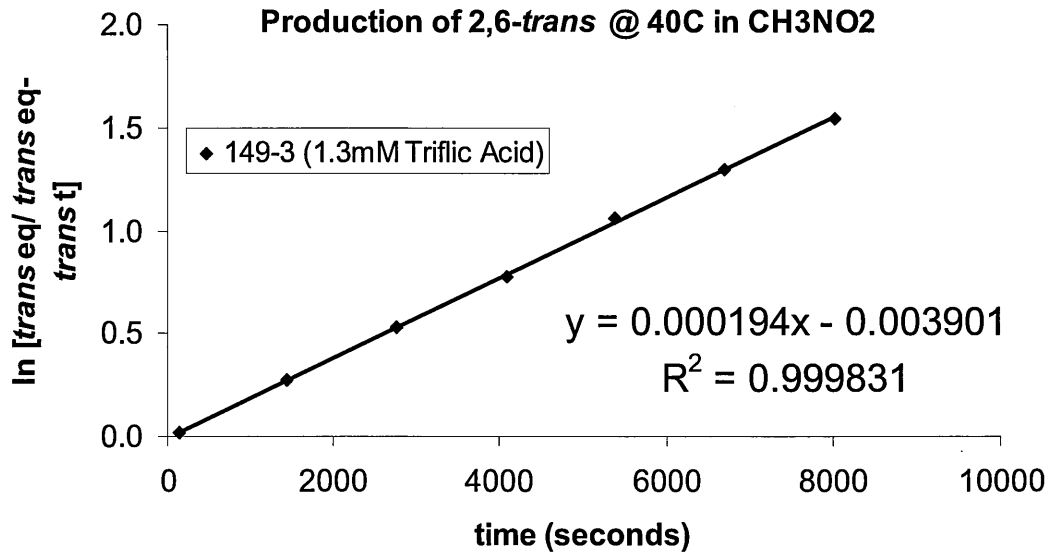


Figure A.8 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.91 mM trifluoromethanesulphonic acid in nitromethane at 40°C



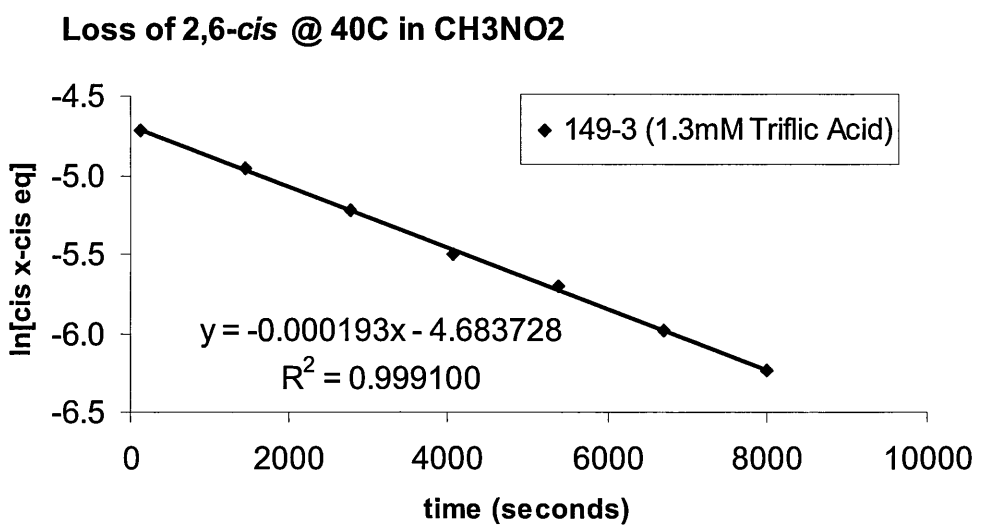


Figure A.9 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.3 mM trifluoromethanesulphonic acid in nitromethane at 40°C

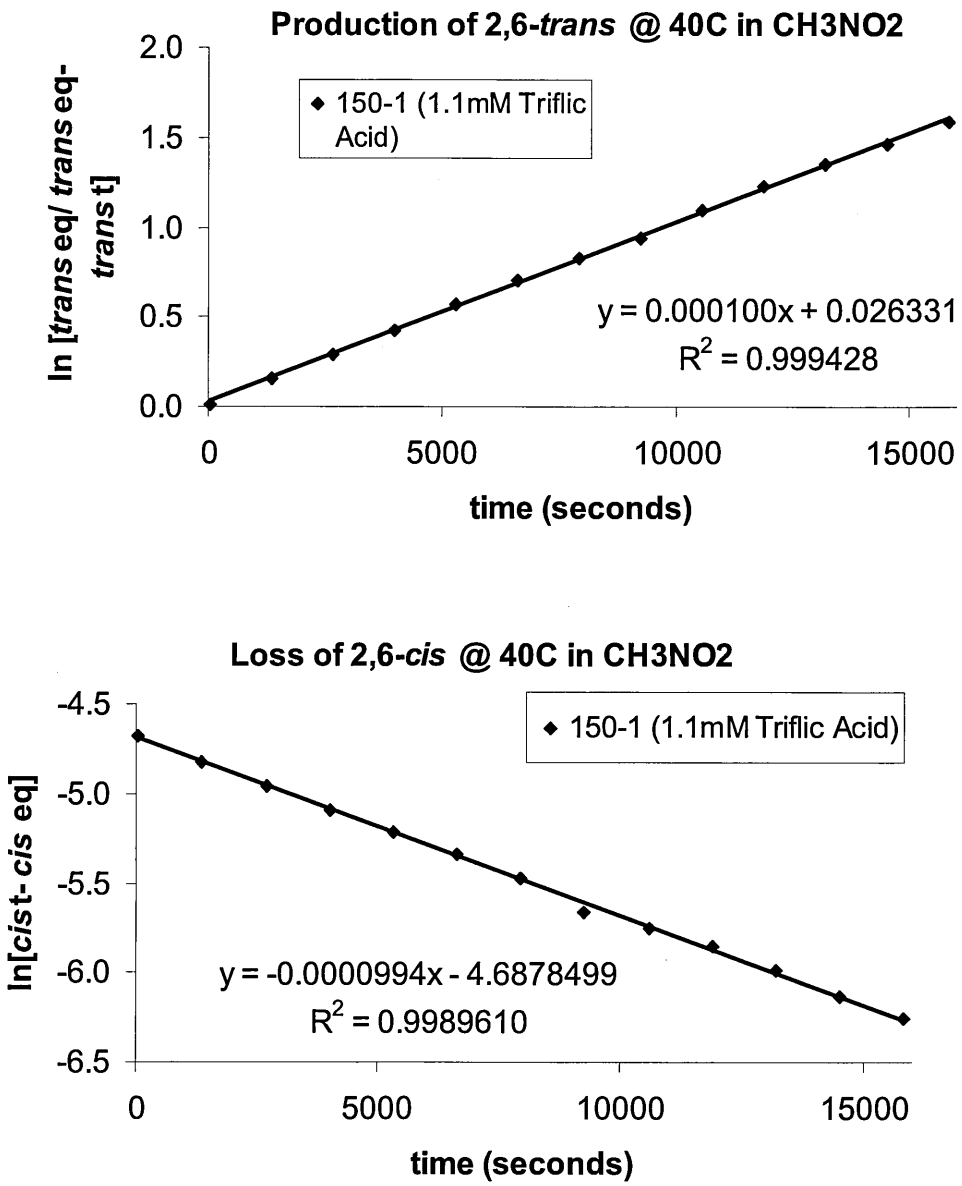


Figure A.10 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.1 mM trifluoromethanesulphonic acid in nitromethane at 40°C

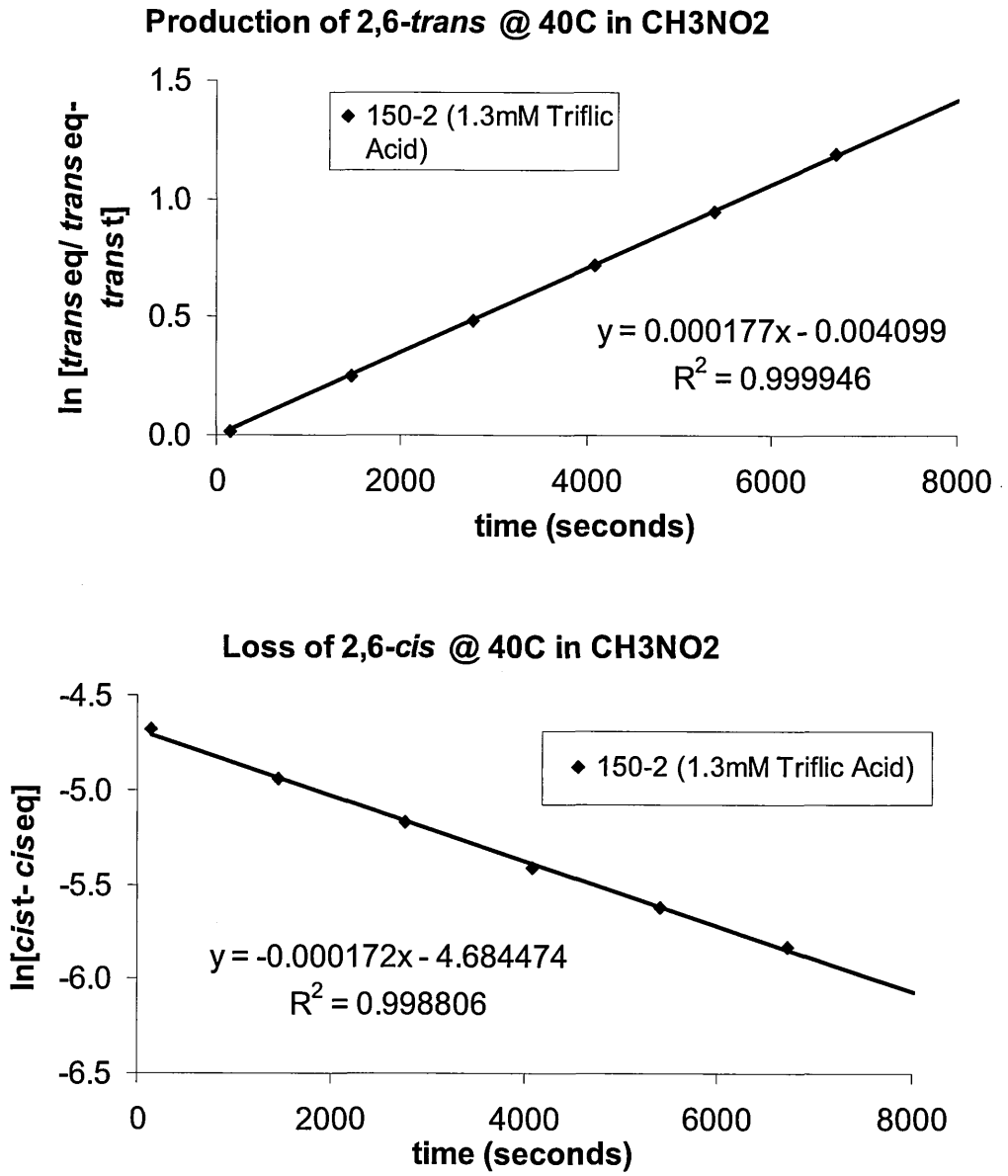


Figure A.11 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.3 mM trifluoromethanesulphonic acid in nitromethane at 40°C

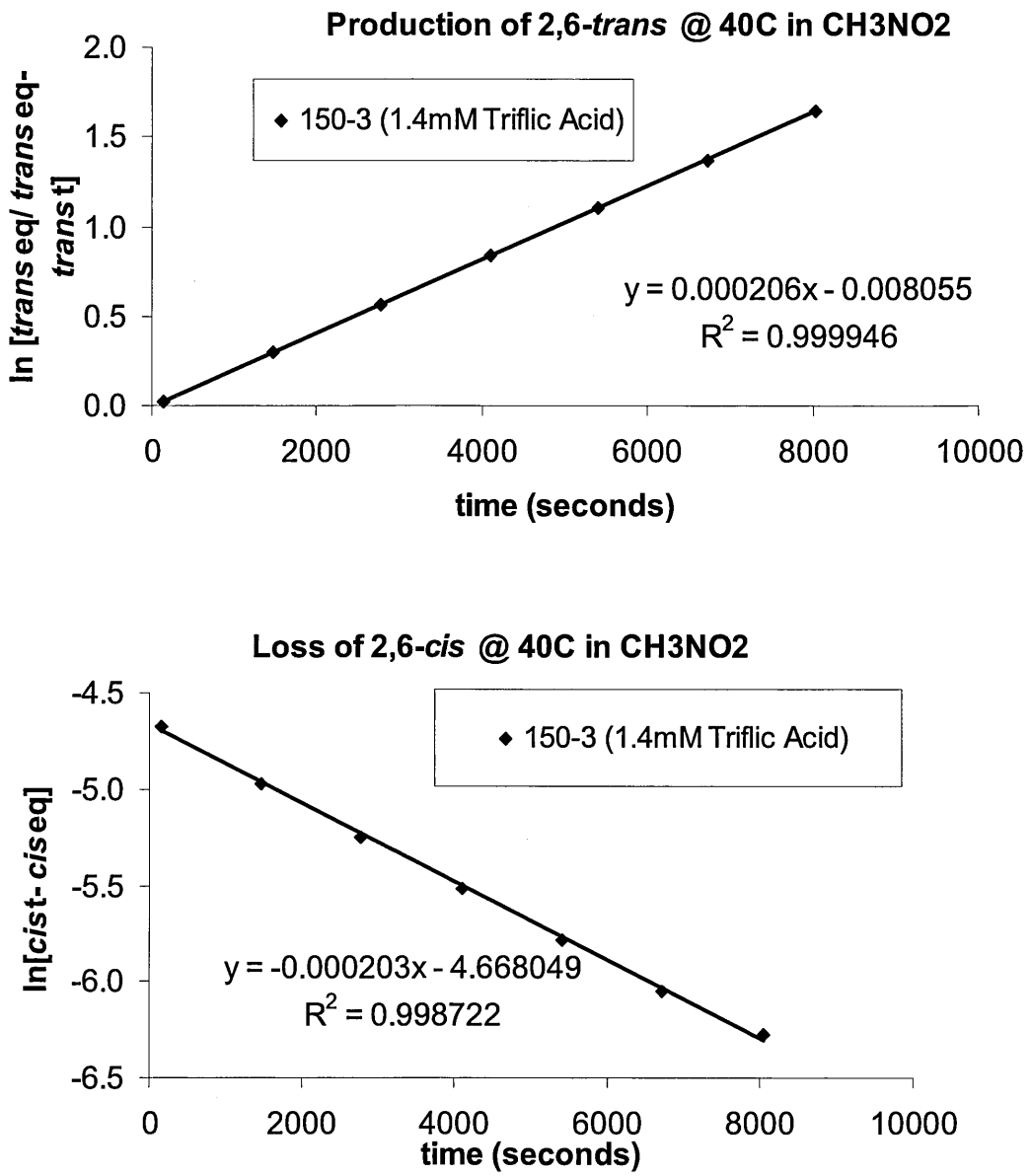


Figure A.12 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.4 mM trifluoromethanesulphonic acid in nitromethane at 40°C

151-3 (1.0mM Triflic Acid)	time (sec)	0	63	1377	2695	4013	5333	6652	7972	9292
	% 2,6-*trans*	0	0.5	7.1	12.4	16.9	20.9	24.3	27.3	29.9
area Naphthalene			689.5	707.6	696.0	693.0	696.1	694.7	693.9	697.2
area 2,6-*cis*			952.3	907.2	847.3	801.5	766.3	731.2	699.8	681.8
area 2,6-*trans*			5.2	69.0	119.7	163.3	202.2	235.2	263.1	291.0
Conc. 2,6-*cis*	(mol/L)		0.0188	0.0174	0.0165	0.0157	0.0149	0.0143	0.0137	0.0133
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0013	0.0023	0.0032	0.0039	0.0046	0.0051	0.0057
ln [*trans* eq/*trans* eq-*trans* t]			0.0108	0.1493	0.2804	0.4081	0.5328	0.6566	0.7746	0.9001
ln [*cis* t -*cis* eq]			-4.672	-4.827	-4.943	-5.066	-5.194	-5.320	-5.450	-5.552
cis + *trans*	(mol/L)		0.0189	0.0187	0.0189	0.0189	0.0189	0.0189	0.0188	0.0189

151-3 (1.0mM Triflic Acid)	time (sec)	10614	11933	14572	17210	19848	27764	54131	127925
	% 2,6-*trans*	32.2	34.1	37.4	39.8	41.7	45.1	48.6	49.5
area Naphthalene		696.5	694.3	693.7	694.3	693.1	693.9	688.4	688.1
area 2,6-*cis*		661.3	632.4	604.5	584.1	562.4	527.9	488.4	478.5
area 2,6-*trans*		313.9	327.8	360.5	385.6	401.6	433.6	461.3	469.5
Conc. 2,6-*cis*	(mol/L)	0.0129	0.0124	0.0118	0.0114	0.0110	0.0103	0.0096	0.0094
Conc. 2,6-*trans*	(mol/L)	0.0061	0.0064	0.0071	0.0075	0.0079	0.0085	0.0091	0.0093
ln [*trans* eq/*trans* eq-*trans* t]		1.0239	1.1126	1.3429	1.5591	1.7366	2.1937	3.0535	3.5122
ln [*cis* t -*cis* eq]		-5.657	-5.820	-6.019	-6.203	-6.426	-6.980	-8.361	-10.061
cis + *trans*	(mol/L)	0.0190	0.0188	0.0189	0.0190	0.0189	0.0188	0.0187	0.0187

Table A.14 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.0 mM trifluoromethanesulphonic acid in nitromethane at 50°C

152-3 (1.1mM Triflic Acid)	time (sec)	0	330	1646	2960	4277	5592	6908	8225	9541	10857	12173
	% 2,6-*trans*	0	1.9	7.8	12.8	17.3	21.1	24.5	27.4	30.1	32.2	34.2
area Naphthalene			705.3	707.9	706.2	701.8	698.5	696.5	701.3	699.7	698.8	701.8
area 2,6-*cis*			951.5	894.6	840.4	791.1	749.2	711.9	692.2	666.0	643.7	628.1
area 2,6-*trans*			18.2	76.1	123.9	165.0	200.5	230.9	261.8	286.3	306.1	326.3
Conc. 2,6-*cis*	(mol/L)		0.0183	0.0172	0.0162	0.0153	0.0146	0.0139	0.0134	0.0129	0.0125	0.0122
Conc. 2,6-*trans*	(mol/L)		0.0004	0.0015	0.0024	0.0032	0.0039	0.0045	0.0051	0.0056	0.0059	0.0063
ln [*trans* eq/*trans* eq-*trans* t]			0.0386	0.1718	0.2978	0.4233	0.5471	0.6668	0.7941	0.9180	1.0301	1.1474
ln [*cis* t -*cis* eq]			-4.6974	-4.8333	-4.9677	-5.0984	-5.2279	-5.3646	-5.4720	-5.5927	-5.7113	-5.8250
cis + *trans*	(mol/L)		0.0187	0.0186	0.0185	0.0185	0.0185	0.0184	0.0185	0.0185	0.0185	0.0185

152-3 (1.1mM Triflic Acid)	time (sec)	13489	14805	16122	17438	20068	22699	27961	33227	41128	67471	110827
	% 2,6-*trans*	35.8	37.3	38.6	39.7	41.6	43.0	45.1	46.4	47.7	49.1	49.6
area Naphthalene		698.7	701.8	705.8	698.0	700.9	697.3	699.3	697.1	690.4	687.3	683.4
area 2,6-*cis*		611.8	599.1	585.8	573.1	557.9	541.4	523.1	507.6	492.9	475.9	468.8
area 2,6-*trans*		341.6	356.3	368.5	377.7	397.6	408.6	428.9	440.0	448.8	459.6	461.6
Conc. 2,6-*cis*	(mol/L)	0.0119	0.0116	0.0113	0.0111	0.0108	0.0105	0.0102	0.0099	0.0097	0.0094	0.0093
Conc. 2,6-*trans*	(mol/L)	0.0066	0.0069	0.0071	0.0073	0.0077	0.0080	0.0083	0.0086	0.0088	0.0091	0.0092
ln [*trans* eq/*trans* eq-*trans* t]		1.2648	1.3676	1.4543	1.5816	1.7883	1.9676	2.3062	2.6115	3.0852	3.9983	4.7737
ln [*cis* t -*cis* eq]		-5.9182	-6.0357	-6.1801	-6.2404	-6.4324	-6.6128	-6.9512	-7.2822	-7.6120	-8.5056	-9.0713
cis + *trans*	(mol/L)	0.0185	0.0185	0.0184	0.0185	0.0185	0.0185	0.0185	0.0185	0.0185	0.0185	0.0185

Table A.15 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.1 mM trifluoromethanesulphonic acid in nitromethane at 50°C

153-1 (1.2mM Triflic Acid)	time (sec)	0	33	1348	2661	3977	5292	6606	7921
	% 2,6-*trans*	0	0.7	8.4	14.7	20.0	24.6	28.4	31.6
area Naphthalene			681.0	687.4	685.9	686.4	688.3	687.9	690.4
area 2,6-*cis*			938.2	868.8	808.2	758.7	716.1	674.7	650.6
area 2,6-*trans*			7.0	80.1	139.4	190.2	233.4	267.6	300.6
Conc. 2,6-*cis*	(mol/L)		0.0187	0.0172	0.0160	0.0150	0.0141	0.0133	0.0128
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0016	0.0028	0.0038	0.0046	0.0053	0.0059
ln [*trans* eq/*trans* eq-*trans* t]			0.0150	0.1854	0.3498	0.5149	0.6782	0.8323	1.0006
ln [*cis* t -*cis* eq]			-4.6716	-4.8521	-5.0131	-5.1745	-5.3439	-5.5294	-5.6705
cis + *trans*	(mol/L)		0.0188	0.0187	0.0188	0.0188	0.0187	0.0186	0.0187

153-1 (1.2mM Triflic Acid)	time (sec)	9236	10549	11864	13177	15806	21064	34194	76271
	% 2,6-*trans*	34.3	36.5	38.5	40.0	42.5	45.7	48.7	50.0
area Naphthalene		681.8	693.8	686.1	685.4	686.5	683.2	681.0	678.1
area 2,6-*cis*		617.5	600.7	581.1	564.5	541.6	512.0	477.6	461.0
area 2,6-*trans*		322.1	345.8	363.1	377.1	401.0	430.6	453.2	461.9
Conc. 2,6-*cis*	(mol/L)	0.0123	0.0118	0.0115	0.0112	0.0107	0.0102	0.0095	0.0092
Conc. 2,6-*trans*	(mol/L)	0.0064	0.0068	0.0072	0.0075	0.0079	0.0086	0.0090	0.0092
ln [*trans* eq/*trans* eq-*trans* t]		1.1587	1.2868	1.4636	1.6046	1.8860	2.4691	3.3959	4.5334
ln [*cis* t -*cis* eq]		-5.8265	-6.0295	-6.1419	-6.3014	-6.5982	-7.0986	-8.6610	#NUM!
cis + *trans*	(mol/L)	0.0187	0.0185	0.0187	0.0187	0.0186	0.0187	0.0186	0.0185

Table A.16 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.2 mM trifluoromethanesulphonic acid in nitromethane at 50°C

153-2 (1.3mM Triflic Acid)	time (sec)	0	41	1352	2666	3981	5294	6608	7921	9235
	% 2,6-*trans*	0	0.9	12.3	20.8	27.5	32.6	36.4	39.5	41.8
area Naphthalene			691.8	690.9	696.2	700.8	695.8	690.3	694.9	697.6
area 2,6-*cis*			946.4	838.3	755.7	695.9	645.3	604.2	578.2	557.9
area 2,6-*trans*			9.0	117.3	198.9	263.4	311.5	346.4	376.8	400.4
Conc. 2,6-*cis*	(mol/L)		0.01858	0.01648	0.01474	0.01348	0.01259	0.01189	0.01130	0.01086
Conc. 2,6-*trans*	(mol/L)		0.00018	0.00231	0.00388	0.00510	0.00608	0.00681	0.00736	0.00779
ln [*trans* eq/*trans* eq-*trans* t]			0.01907	0.28312	0.53599	0.78934	1.05031	1.30481	1.54875	1.79318
ln [*cis* t -*cis* eq]			-4.6749	-4.9301	-5.2049	-5.4646	-5.7008	-5.9388	-6.1906	-6.4317
cis + *trans*	(mol/L)		0.0188	0.0188	0.0186	0.0186	0.0187	0.0187	0.0187	0.0187

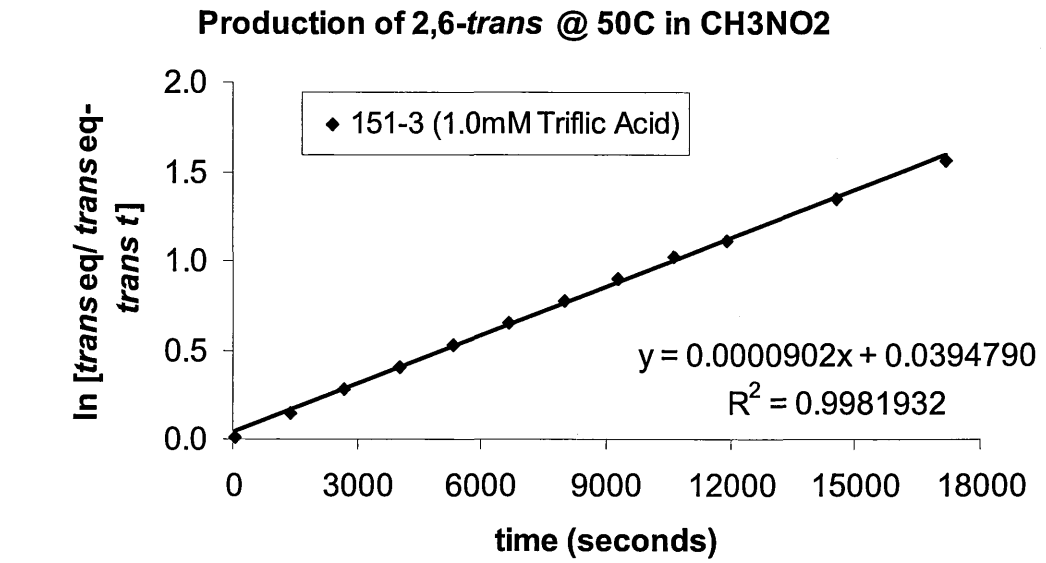
153-2 (1.3mM Triflic Acid)	time (sec)	10550	11864	13180	14495	18438	25013	34213	127599
	% 2,6-*trans*	43.6	45.0	46.1	46.9	48.5	49.6	50.1	50.4
area Naphthalene		696.5	695.2	690.6	692.1	693.8	701.7	697.1	701.6
area 2,6-*cis*		539.5	523.8	510.3	505.0	488.1	481.4	472.6	468.7
area 2,6-*trans*		416.6	428.1	435.8	446.2	459.6	474.3	474.7	475.4
Conc. 2,6-*cis*	(mol/L)	0.01052	0.01023	0.01003	0.00991	0.00955	0.00932	0.00921	0.00907
Conc. 2,6-*trans*	(mol/L)	0.00812	0.00836	0.00857	0.00875	0.00900	0.00918	0.00925	0.00920
ln [*trans* eq/*trans* eq-*trans* t]		2.03001	2.24728	2.48247	2.75358	3.27164	3.99806	4.50621	4.13928
ln [*cis* t -*cis* eq]		-6.6703	-6.9268	-7.1514	-7.3262	-8.1017	-9.6287	#NUM!	#NUM!
cis + *trans*	(mol/L)	0.0186	0.0186	0.0186	0.0187	0.0185	0.0185	0.0185	0.0183

Table A.17 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.3 mM trifluoromethanesulphonic acid in nitromethane at 50°C

159-2 (0.43mM Triflic Acid)	time (sec)	0	49	2677	5310	7943
	% 2,6-*trans*	0	1.3	31.2	42.5	46.9
area Naphthalene			701.9	703.3	702.0	703.1
area 2,6-*cis*			952.9	661.6	553.1	508.4
area 2,6-*trans*			12.2	300.1	408.0	448.7
Conc. 2,6-*cis*	(mol/L)		0.01843	0.01277	0.01070	0.00982
Conc. 2,6-*trans*	(mol/L)		0.00024	0.00579	0.00789	0.00867
ln [*trans* eq/*trans* eq-*trans* t]			0.02557	0.96679	1.85834	2.61478
ln [*cis* t -*cis* eq]			-4.690	-5.648	-6.537	-7.472
cis + *trans*	(mol/L)		0.0187	0.0186	0.0186	0.0185

		1/9/04 4:50pm										
159-3 (0.37mM Triflic Acid)	time (sec)	0	41	2668	5301	7930	10558	13186	15813	18440	31557	126258
	% 2,6-*trans*	0	0.7	22.7	34.3	40.7	44.3	46.5	47.8	48.6	50.0	50.4
area Naphthalene			686.8	698.1	686.7	690.3	689.6	693.2	691.1	699.8	692.8	701.2
area 2,6-*cis*			949.8	739.8	620.0	566.8	528.9	510.5	497.6	485.5	475.3	447.8
area 2,6-*trans*			7.1	217.6	323.3	388.5	421.2	443.1	456.3	459.6	475.6	454.3
Conc. 2,6-*cis*	(mol/L)		0.0188	0.0144	0.0123	0.0111	0.0104	0.0100	0.0098	0.0094	0.0093	0.0087
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0042	0.0064	0.0076	0.0083	0.0087	0.0090	0.0089	0.0093	0.0088
ln [*trans* eq/*trans* eq-*trans* t]			0.0150	0.5983	1.1398	1.6767	2.1398	2.5689	3.0743	2.9707	4.7893	2.7476
ln [*cis* t -*cis* eq]			-4.6640	-5.2903	-5.8396	-6.3202	-6.8452	-7.3384	-7.7587	-9.5576	#NUM!	#NUM!
cis + *trans*	(mol/L)		0.0189	0.0186	0.0187	0.0188	0.0187	0.0187	0.0187	0.0183	0.0186	0.0175

Table A.18 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.43 (159-2) or 0.37 (159-3) mM trifluoromethanesulphonic acid in nitromethane at 50°C



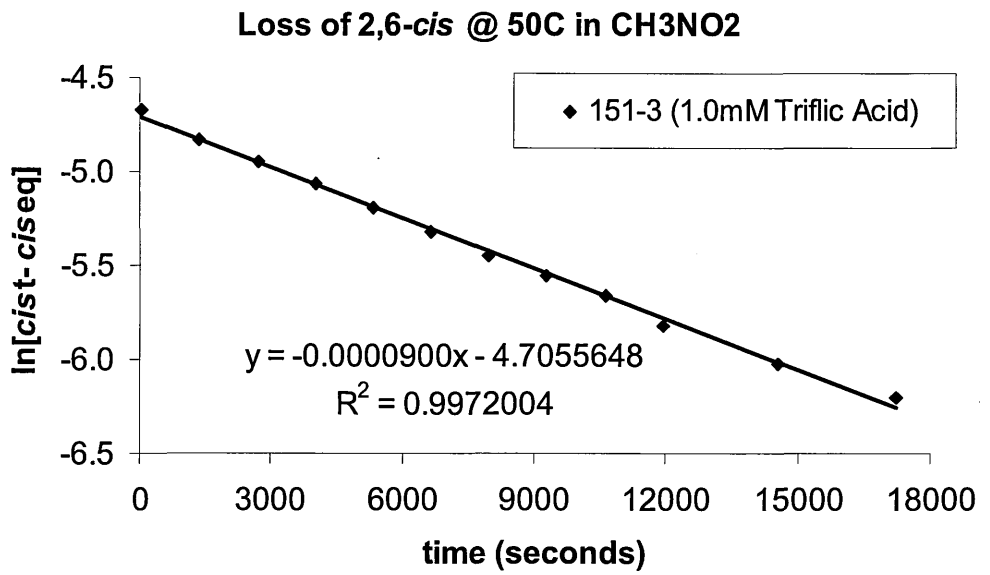


Figure A.13 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.0 mM trifluoromethanesulphonic acid in nitromethane at 50°C

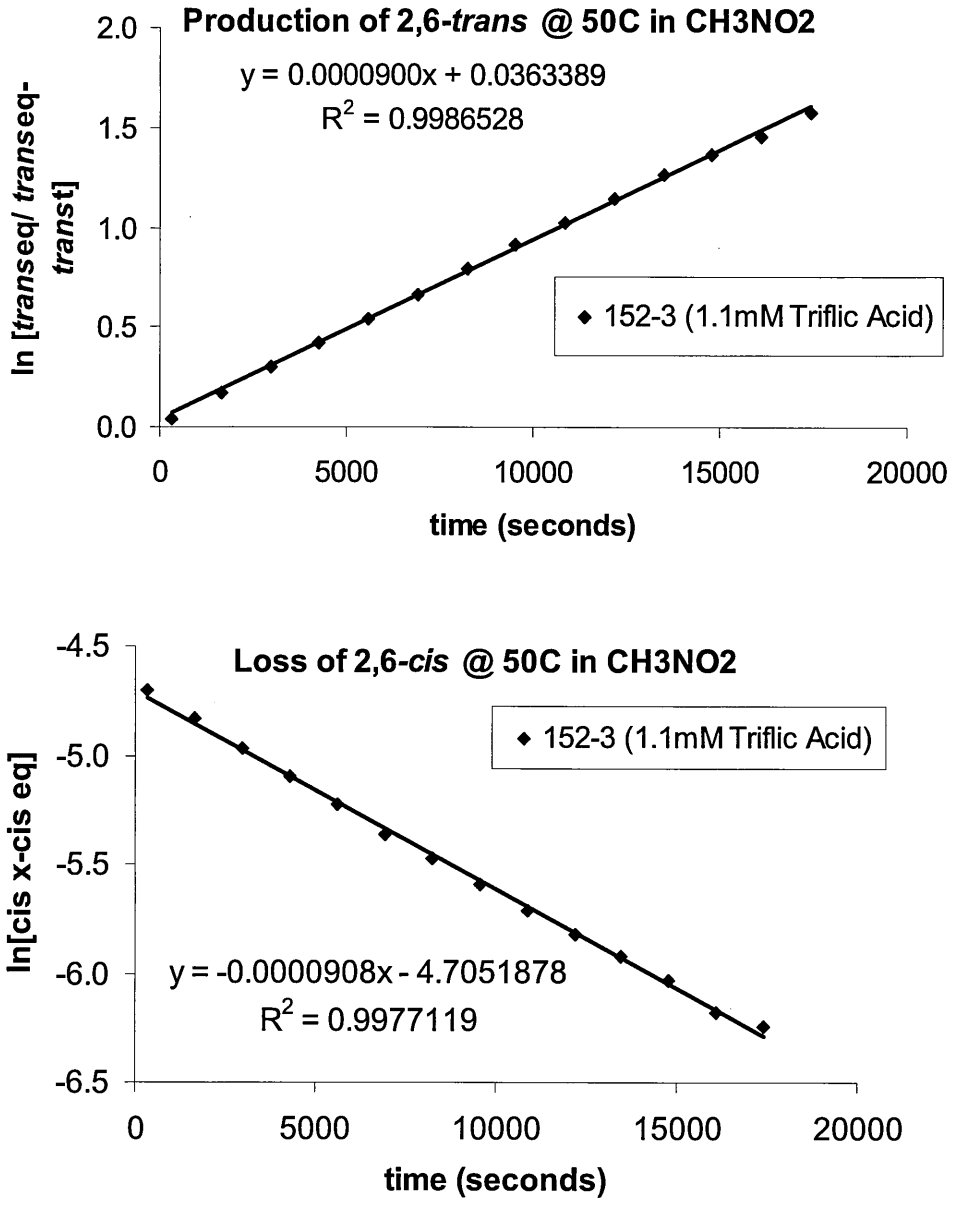


Figure A.14 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.1 mM trifluoromethanesulphonic acid in nitromethane at 50°C

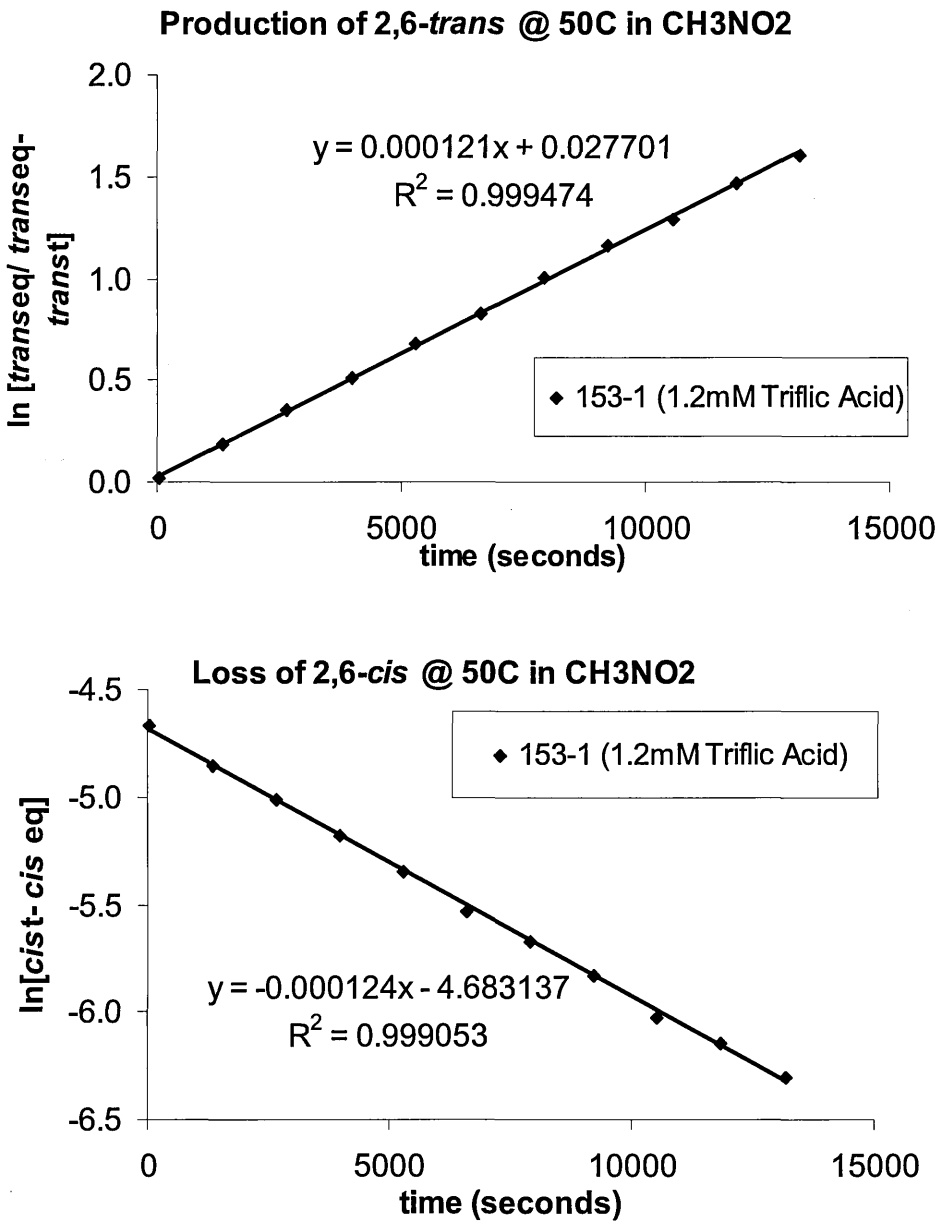


Figure A.15 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.2 mM trifluoromethanesulphonic acid in nitromethane at 50°C

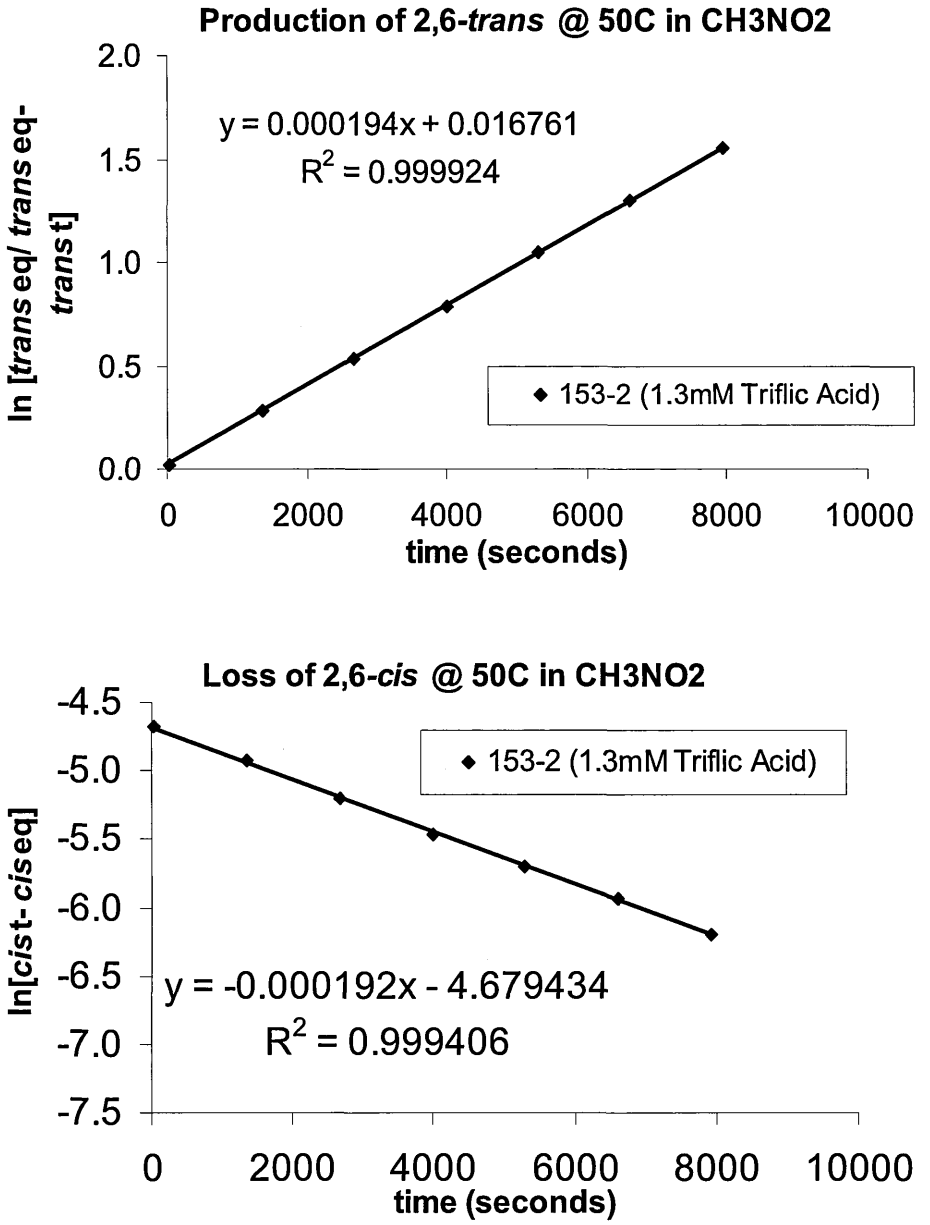
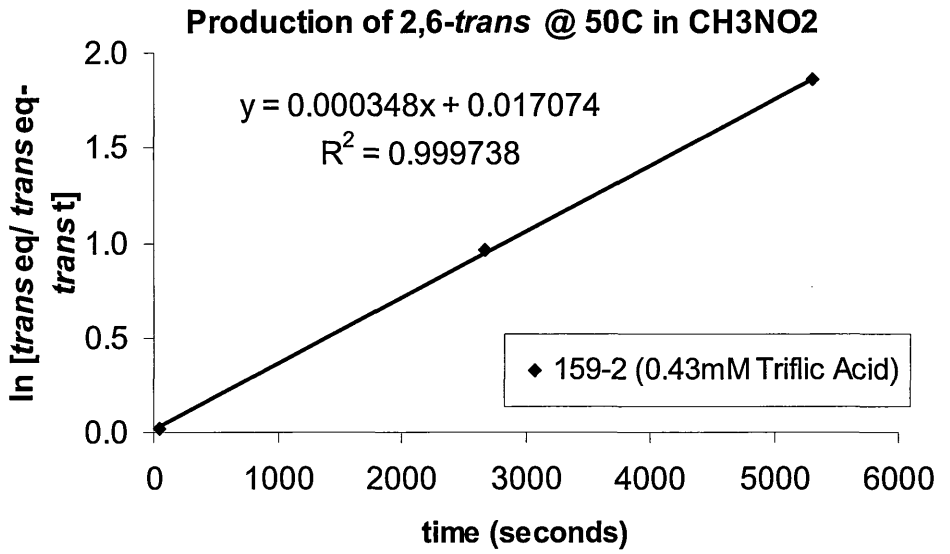


Figure A.16 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.3 mM trifluoromethanesulphonic acid in nitromethane at 50°C



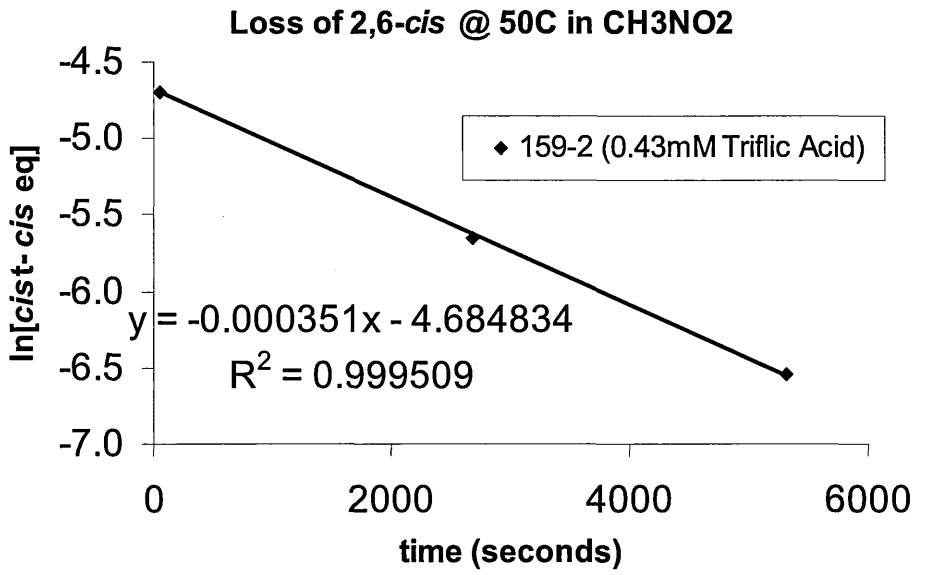


Figure A.17 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.43 mM trifluoromethanesulphonic acid in nitromethane at 50°C

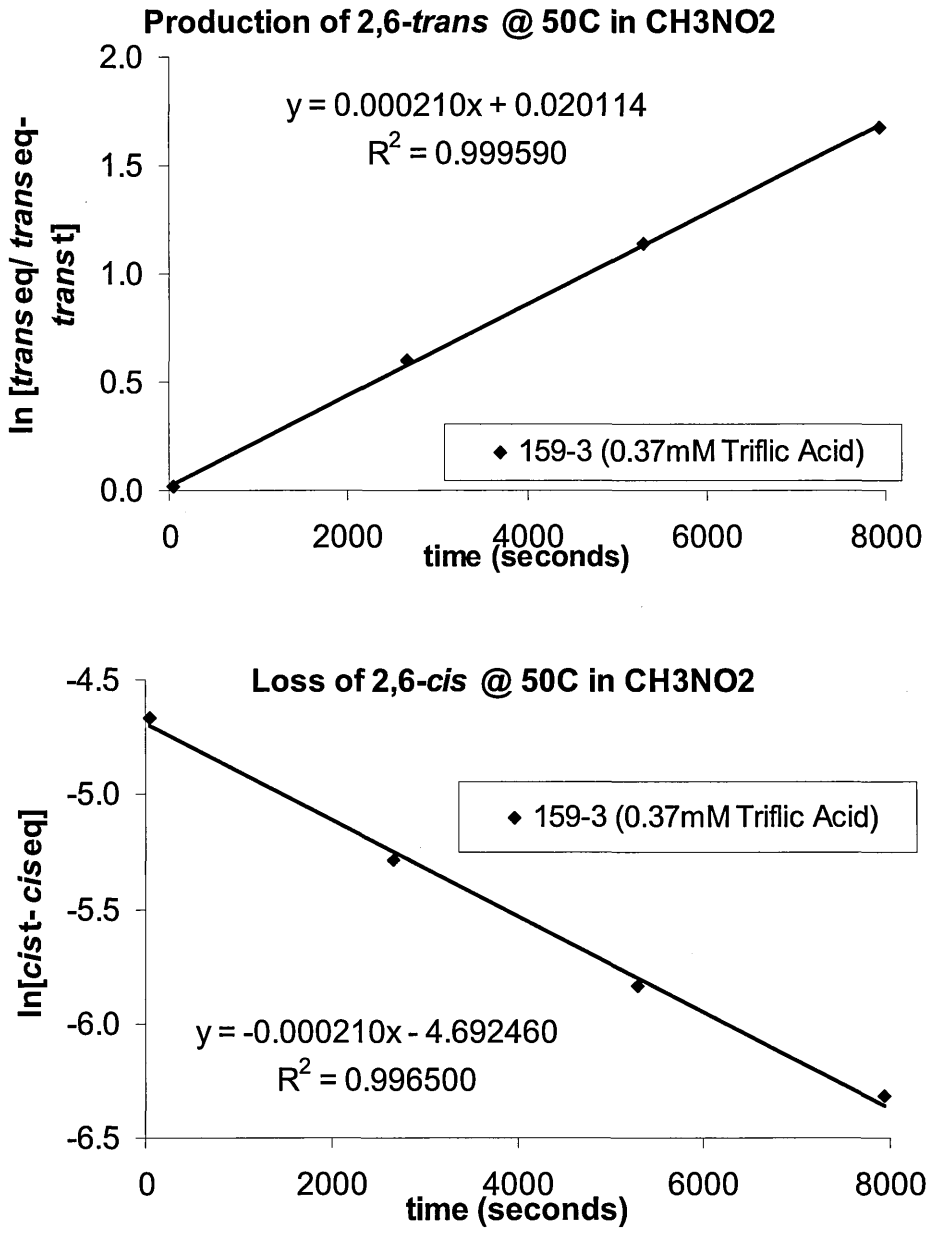


Figure A.18 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.37 mM trifluoromethanesulphonic acid in nitromethane at 50°C

155-3 (0.8mM Triflic Acid)	time (sec)	0	76	1390	2705	4022	5340	80660
	% 2,6-*trans*	0	1.2	39.6	47.9	49.7	50.2	50.3
area Naphthalene			684.3	691.1	697.1	685.8	688.3	672.8
area 2,6-*cis*			941.8	571.9	494.9	468.2	462.1	408.1
area 2,6-*trans*			11.8	375.0	455.1	462.9	465.1	413.3
Conc. 2,6-*cis*	(mol/L)		0.0187	0.0112	0.0096	0.0093	0.0091	0.0082
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0074	0.0089	0.0092	0.0092	0.0083
ln [*trans* eq/*trans* eq-*trans* t]			0.0255	1.5715	3.0624	4.2361	4.3143	2.2724
ln [*cis* t -*cis* eq]			-4.658	-6.196	-7.728	-9.561	#NUM!	#NUM!
cis + *trans*	(mol/L)		0.0189	0.0186	0.0185	0.0184	0.0183	0.0166

		12/10/03 5:00pm										
155-4 (0.64mM Triflic Acid)	time (sec)	0	59	1375	2694	4013	5335	6654	7974	9294	10614	11934
	% 2,6-*trans*	0	1.2	26.1	38.2	43.9	46.8	48.3	49.2	49.6	49.8	50.0
area Naphthalene			681.6	678.3	684.0	678.3	676.8	688.5	679.4	684.2	682.6	681.7
area 2,6-*cis*			933.2	693.1	584.2	528.2	500.9	488.8	478.0	470.0	473.7	470.4
area 2,6-*trans*			11.1	245.2	360.8	413.1	440.9	456.3	462.3	462.5	470.8	471.1
Conc. 2,6-*cis*	(mol/L)		0.0186	0.0139	0.0116	0.0106	0.0100	0.0096	0.0096	0.0093	0.0094	0.0094
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0049	0.0072	0.0083	0.0088	0.0090	0.0092	0.0092	0.0094	0.0094
ln [*trans* eq/*trans* eq-*trans* t]			0.0237	0.7328	1.4186	2.0804	2.7502	3.0431	3.8059	3.5516	4.7184	4.9634
ln [*cis* t -*cis* eq]			-4.689	-5.409	-6.120	-6.747	-7.339	-8.333	-8.781	#NUM!	-10.667	#NUM!
cis + *trans*	(mol/L)		0.0188	0.0188	0.0188	0.0188	0.0189	0.0186	0.0188	0.0185	0.0188	0.0188

		12/11/03 2:15pm										
156-1 (0.49mM Triflic Acid)	time (sec)	0	51	1364	2681	5318	9272	11904	15861	21134	29045	42272
	% 2,6-*trans*	0	0.4	4.3	6.8	10.4	14.0	15.7	17.6	19.4	21.0	22.2
area Naphthalene			685.3	689.8	696.0	690.2	696.5	691.8	695.5	705.2	702.7	703.2
area 2,6-*cis*			954.4	915.0	899.2	855.1	827.0	811.0	796.5	780.4	767.3	757.9
area 2,6-*trans*			4.2	40.7	65.6	99.4	134.8	151.4	170.6	187.6	203.9	216.6
Conc. 2,6-*cis*	(mol/L)		0.0189	0.0180	0.0175	0.0168	0.0161	0.0159	0.0156	0.0150	0.0148	0.0146
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0008	0.0013	0.0020	0.0026	0.0030	0.0033	0.0036	0.0039	0.0042
ln [*trans* eq/*trans* eq-*trans* t]			0.0088	0.0881	0.1447	0.2305	0.3238	0.3752	0.4317	0.4784	0.5357	0.5803
ln [*cis* t -*cis* eq]			-4.666	-4.766	-4.823	-4.917	-5.017	-5.049	-5.108	-5.198	-5.235	-5.272
cis + *trans*	(mol/L)		0.0190	0.0188	0.0188	0.0188	0.0188	0.0189	0.0189	0.0186	0.0188	0.0188

Table A.19 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.8 (155-3), 0.64 (155-4), or 0.49 (156-1) mM trifluoromethanesulphonic acid in nitromethane at 60°C

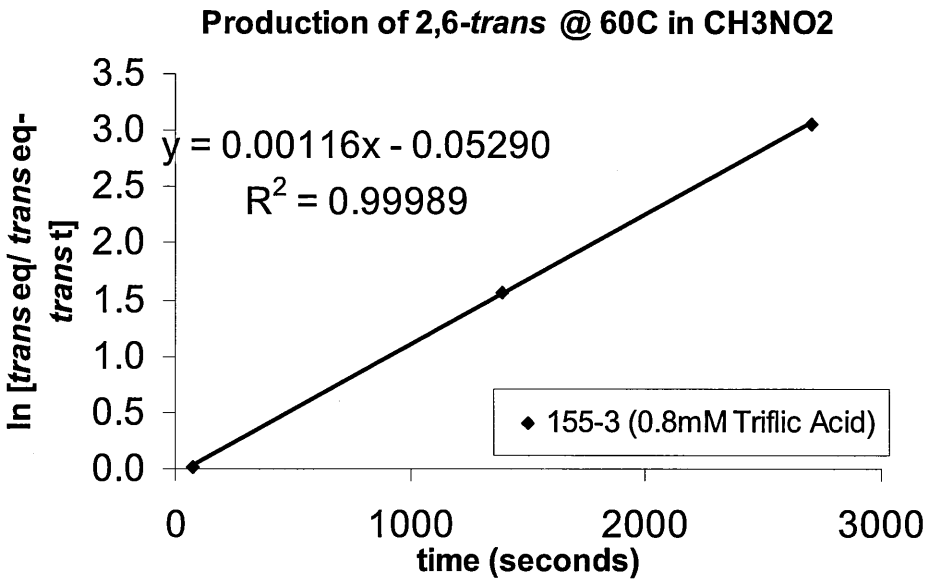
160-3 Triflic Acid	time (sec)	0	46	1362	2679	5311	7945	10578	13211	15844	18478
	% 2,6-trans	0	0.5	4.0	6.9	11.5	15.0	17.9	20.3	22.4	24.1
area Naphthalene			710.0	711.0	709.8	710.2	711.7	713.0	713.5	714.7	709.5
area 2,6-*cis*			990.8	948.2	917.1	870.8	838.4	809.7	787.5	768.3	745.5
area 2,6-*trans*			4.6	39.6	68.0	112.9	148.4	176.7	200.5	221.3	237.0
Conc. 2,6-*cis*	(mol/L)		0.0189	0.0181	0.0175	0.0166	0.0160	0.0154	0.0150	0.0146	0.0143
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0008	0.0013	0.0022	0.0028	0.0034	0.0038	0.0042	0.0045
ln [*trans* eq/*trans* eq-*trans* x]			0.0093	0.0830	0.1473	0.2578	0.3539	0.4373	0.5136	0.5845	0.6491
ln [*cis-cis* eq]			-4.6618	-4.7549	-4.8227	-4.9407	-5.0365	-5.1293	-5.2053	-5.2790	-5.3458
cis + *trans*	(mol/L)		0.0190	0.0189	0.0188	0.0188	0.0188	0.0188	0.0188	0.0188	0.0188

160-3 Triflic Acid	time (sec)	30331	35599	40866	48771	58005	59323	69873	83062	101532	127942
	% 2,6-trans	29.7	31.5	32.8	34.3	35.7	35.8	36.8	37.6	38.1	38.4
area Naphthalene		699.9	708.5	706.7	704.5	706.2	701.1	703.8	693.0	690.4	685.9
area 2,6-*cis*		687.5	673.7	657.1	638.4	627.2	623.2	615.5	606.3	595.7	587.0
area 2,6-*trans*		290.9	309.1	320.2	333.8	348.1	348.2	358.3	364.7	366.5	366.5
Conc. 2,6-*cis*	(mol/L)	0.0133	0.0129	0.0126	0.0123	0.0121	0.0121	0.0119	0.0119	0.0117	0.0116
Conc. 2,6-*trans*	(mol/L)	0.0056	0.0059	0.0062	0.0064	0.0067	0.0067	0.0069	0.0071	0.0072	0.0073
ln [*trans* eq/*trans* eq-*trans* x]		0.9016	0.9771	1.0431	1.1309	1.2193	1.2375	1.3008	1.3952	1.4220	1.4429
ln [*cis-cis* eq]		-5.5627	-5.6805	-5.7680	-5.8764	-5.9678	-5.9638	-6.0426	-6.0406	-6.1119	-6.1559
cis + *trans*	(mol/L)	0.0190	0.0188	0.0188	0.0187	0.0188	0.0188	0.0188	0.0190	0.0189	0.0189

Table A.20 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.86 mM trifluoromethanesulphonic acid in nitromethane at 60°C

160-4 (0.93mM Triflic Acid)	time (sec)	0	73	1391	2710	4029	5345	6661	7980	9298	10617	14576
	% 2,6-*trans*	0	1.0	17.0	27.5	34.4	39.0	42.0	44.1	45.6	46.7	48.6
area Naphthalene			712.0	705.7	710.2	709.6	704.9	710.1	716.7	713.2	715.5	709.9
area 2,6-*cis*			981.1	815.9	714.1	643.2	594.9	567.2	551.0	531.2	525.6	503.0
area 2,6-*trans*			9.6	167.4	271.5	337.6	379.6	410.2	435.1	445.2	461.1	475.7
Conc. 2,6-*cis*	(mol/L)		0.0187	0.0157	0.0137	0.0123	0.0115	0.0108	0.0104	0.0101	0.0100	0.0096
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0032	0.0052	0.0065	0.0073	0.0078	0.0082	0.0085	0.0088	0.0091
ln [*trans* eq/*trans* eq-*trans* t]			0.0197	0.4196	0.8035	1.1624	1.5047	1.7986	2.0954	2.3202	2.6728	3.4419
ln [*cis* t -*cis* eq]			-4.6659	-5.0516	-5.4368	-5.8064	-6.1377	-6.4719	-6.7772	-7.1138	-7.3008	-8.0429
cis + *trans*	(mol/L)		0.0189	0.0189	0.0188	0.0188	0.0188	0.0187	0.0187	0.0186	0.0187	0.0187
		1/19/04 4:10pm										
2-1 (0.87mM Triflic Acid)	time (sec)	0	95	1471	2789	4105	5421	6739	8057	9374	10692	12011
	% 2,6-*trans*	0	0.7	9.6	16.3	21.6	25.8	29.2	32.0	34.4	36.3	38.0
area Naphthalene			719.7	718.4	719.3	721.5	719.6	721.4	721.3	715.4	718.6	718.8
area 2,6-*cis*			1000.6	903.6	837.5	785.2	743.0	707.9	676.3	653.1	632.4	616.3
area 2,6-*trans*			7.0	96.3	163.4	216.2	258.5	292.5	318.9	342.4	361.1	378.1
Conc. 2,6-*cis*	(mol/L)		0.0189	0.0171	0.0158	0.0148	0.0140	0.0133	0.0127	0.0124	0.0120	0.0116
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0018	0.0031	0.0041	0.0049	0.0055	0.0060	0.0065	0.0068	0.0071
ln [*trans* eq/*trans* eq-*trans* t]			0.0141	0.2152	0.3977	0.5672	0.7317	0.8812	1.0180	1.1757	1.2943	1.4266
ln [*cis* t -*cis* eq]			-4.6482	-4.8563	-5.0344	-5.2071	-5.3558	-5.5153	-5.6747	-5.7775	-5.9332	-6.0565
cis + *trans*	(mol/L)		0.0190	0.0189	0.0189	0.0188	0.0189	0.0188	0.0187	0.0189	0.0188	0.0188

Table A.21 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.93 (160-4) or 0.87 (2-1) mM trifluoromethanesulphonic acid in nitromethane at 60°C



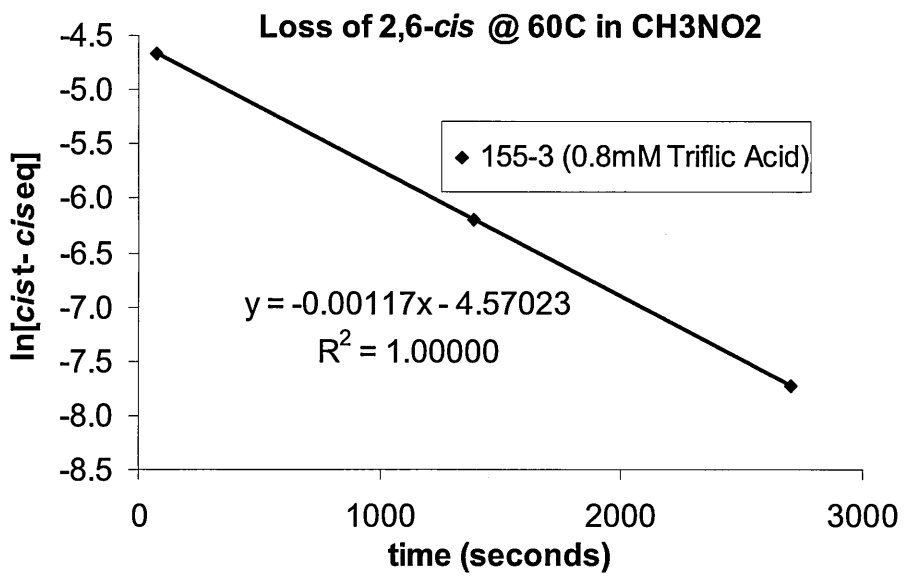
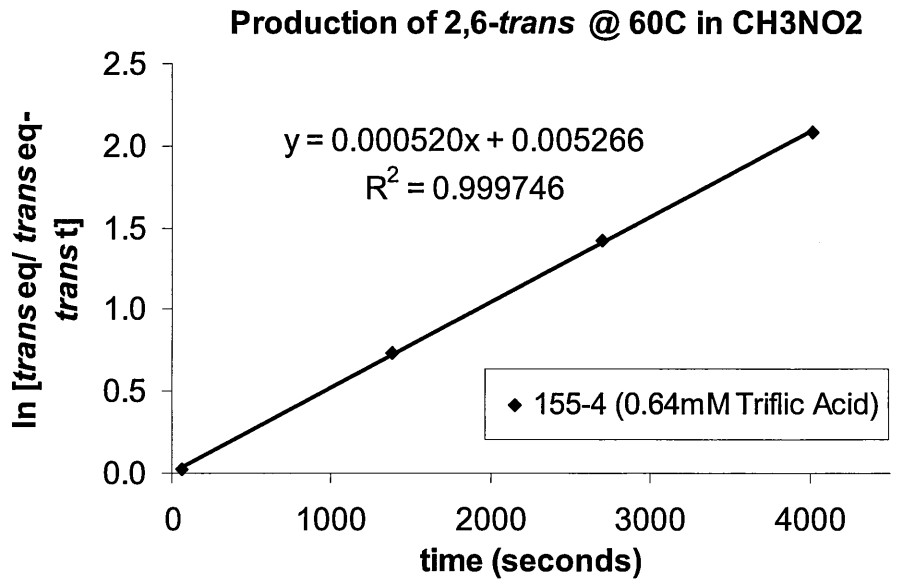


Figure A.19 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.8 mM trifluoromethanesulphonic acid in nitromethane at 60°C



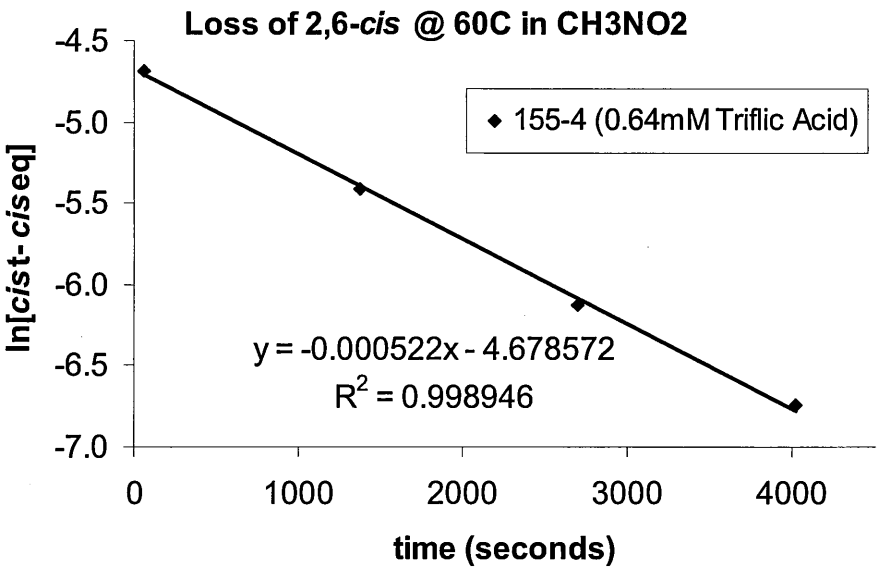


Figure A.20 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.64 mM trifluoromethanesulphonic acid in nitromethane at 60°C

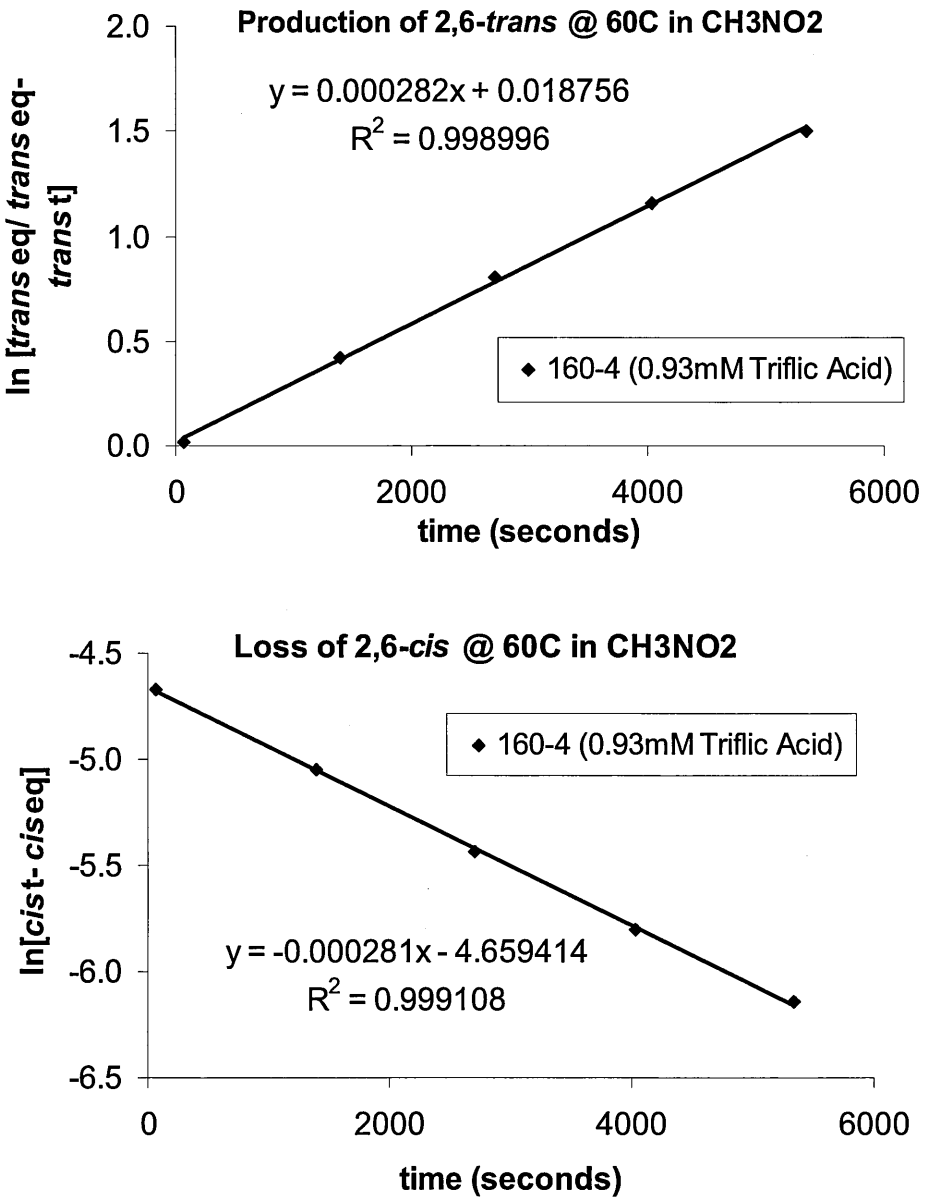


Figure A.21 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.93 mM trifluoromethanesulphonic acid in nitromethane at 60°C

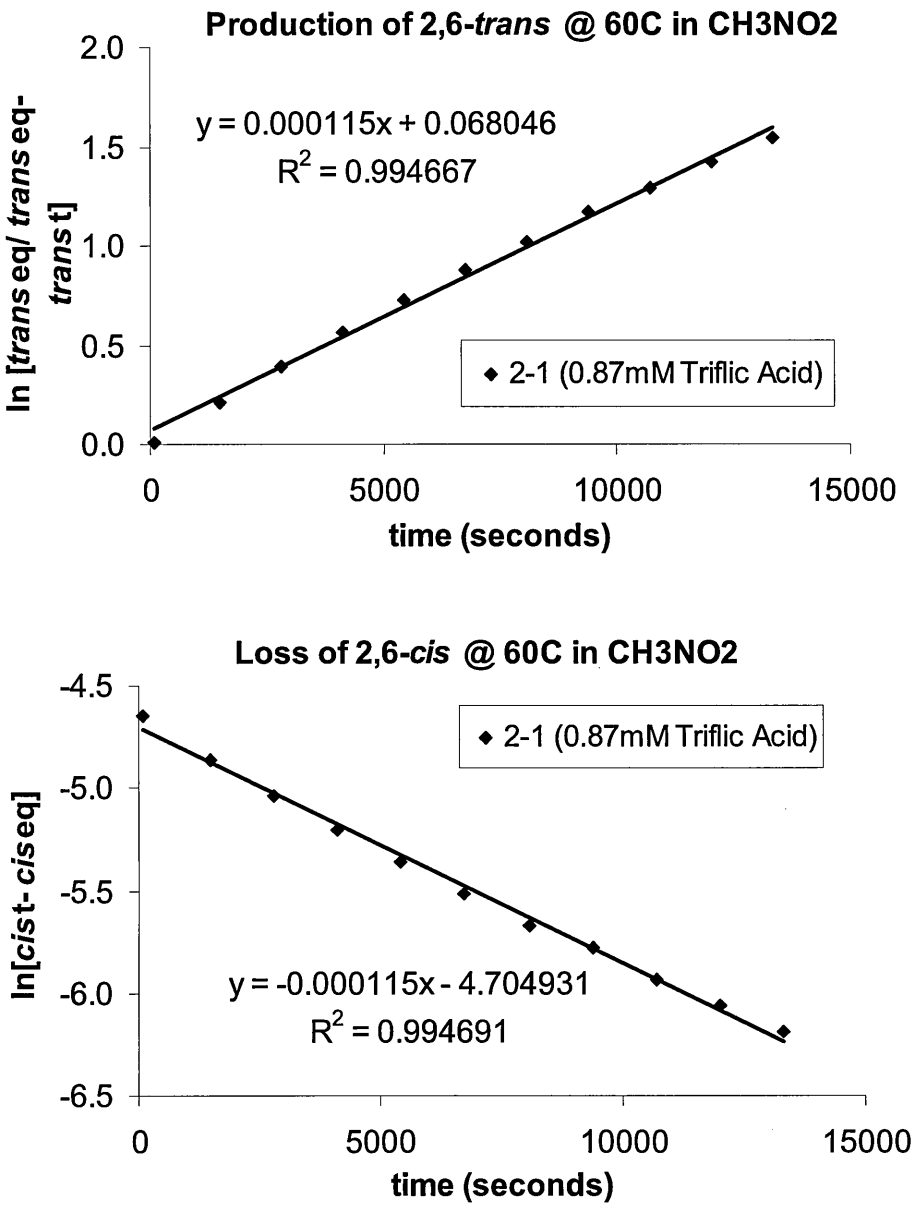


Figure A.22 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.87 mM trifluoromethanesulphonic acid in nitromethane at 60°C

157-3 (0.63mM Triflic Acid)	time (sec)	0	68	1384	2702	4019	5336	6655	7974	9294
	% 2,6-*trans*	0	0.7	12.8	21.0	26.8	31.2	34.5	37.0	39.0
area Naphthalene			695.0	692.9	691.6	693.7	693.0	684.7	694.1	690.5
area 2,6-*cis*			951.0	834.7	754.1	698.3	653.9	621.2	598.4	575.6
area 2,6-*trans*			6.5	122.0	200.3	255.9	296.0	326.6	350.8	367.3
Conc. 2,6-*cis*	(mol/L)		0.0186	0.0164	0.0148	0.0137	0.0128	0.0123	0.0117	0.0113
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0024	0.0039	0.0050	0.0058	0.0065	0.0069	0.0072
ln [*trans* eq/*trans* eq-*trans* t]			0.0137	0.2972	0.5497	0.7735	0.9772	1.1923	1.3392	1.4991
ln [*cis* t -*cis* eq]			-4.6744	-4.9466	-5.1929	-5.4218	-5.6372	-5.7862	-6.0089	-6.1805
cis + *trans*	(mol/L)		0.0187	0.0187	0.0187	0.0187	0.0186	0.0188	0.0186	0.0185

157-3 (0.63mM Triflic Acid)	time (sec)	10612	11931	14568	18525	25121	32918	38331	51549	128110
	% 2,6-*trans*	40.5	41.8	43.7	45.4	47.0	47.8	48.2	48.7	49.0
area Naphthalene		692.6	687.1	693.2	692.1	687.6	694.1	701.6	700.7	768.5
area 2,6-*cis*		562.3	552.2	532.6	513.2	493.3	491.7	488.6	486.0	527.6
area 2,6-*trans*		383.1	396.3	413.2	426.9	437.1	450.1	454.7	461.4	507.8
Conc. 2,6-*cis*	(mol/L)	0.0110	0.0109	0.0104	0.0101	0.0097	0.0096	0.0095	0.0094	0.0093
Conc. 2,6-*trans*	(mol/L)	0.0075	0.0078	0.0081	0.0084	0.0086	0.0088	0.0088	0.0089	0.0090
ln [*trans* eq/*trans* eq-*trans* t]		1.6483	1.8461	2.0428	2.3088	2.6335	2.9342	2.9239	3.2559	3.3464
ln [*cis* t -*cis* eq]		-6.3343	-6.3992	-6.7397	-7.1075	-7.6173	-7.9039	-8.4853	-8.6901	-9.5335
cis + *trans*	(mol/L)	0.0185	0.0187	0.0185	0.0184	0.0184	0.0184	0.0183	0.0184	0.0183

Table A.22 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.63 mM trifluoromethanesulphonic acid in nitromethane at 70°C

158-1 (0.78mM Triflic Acid)	time (sec)	0	76	1387	2703	4018	5334	6650	7967
	% 2,6-*trans*	0	1.0	21.4	32.2	38.3	42.1	44.4	46.0
area Naphthalene			700.2	691.9	702.3	702.0	696.8	703.0	701.9
area 2,6-*cis*			952.5	754.3	649.5	589.1	549.5	529.6	513.0
area 2,6-*trans*			10.1	205.1	308.7	366.3	399.0	423.6	437.5
Conc. 2,6-*cis*	(mol/L)		0.0185	0.0148	0.0126	0.0114	0.0107	0.0102	0.0099
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0040	0.0060	0.0071	0.0078	0.0082	0.0085
ln [*trans* eq/*trans* eq-*trans* t]			0.0214	0.5712	1.0364	1.4524	1.8363	2.1590	2.4653
ln [*cis* t -*cis* eq]			-4.6754	-5.1755	-5.6816	-6.0990	-6.4641	-6.8312	-7.1633
cis + *trans*	(mol/L)		0.0187	0.0188	0.0185	0.0185	0.0185	0.0184	0.0184

158-1 (0.78mM Triflic Acid)	time (sec)	9283	10598	13230	15863	22446	31661	127790
	% 2,6-*trans*	47.1	47.9	48.8	49.3	49.9	50.1	50.2
area Naphthalene		702.9	706.6	708.2	707.2	707.3	706.6	727.8
area 2,6-*cis*		502.8	496.7	488.4	480.9	476.5	472.3	475.2
area 2,6-*trans*		447.9	456.0	465.8	468.4	474.4	474.4	479.9
Conc. 2,6-*cis*	(mol/L)	0.0097	0.0095	0.0094	0.0092	0.0091	0.0091	0.0089
Conc. 2,6-*trans*	(mol/L)	0.0087	0.0088	0.0089	0.0090	0.0091	0.0091	0.0090
ln [*trans* eq/*trans* eq-*trans* t]		2.7400	2.9443	3.3678	3.5862	4.1742	4.2397	3.4412
ln [*cis* t -*cis* eq]		-7.4817	-7.8360	-8.4471	-9.3875	#NUM!	#NUM!	#NUM!
cis + *trans*	(mol/L)	0.0184	0.0183	0.0183	0.0182	0.0183	0.0182	0.0178

Table A.23 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.78 mM trifluoromethanesulphonic acid in nitromethane at 70°C

3-1 (0.82mM Triflic Acid)	time (sec)	0	54	1367	2682	3997	5313	6629	7945	9261	11894	25045
	% 2,6-*trans*	0	0.5	18.8	30.4	37.4	41.7	44.5	46.3	47.5	48.9	50.2
area Naphthalene			749.7	740.8	744.1	748.7	748.2	747.5	745.0	738.5	753.5	756.6
area 2,6-*cis*			1034.9	836.3	717.8	648.0	602.5	575.9	554.6	536.9	526.0	510.5
area 2,6-*trans*			4.8	193.5	313.2	387.1	431.5	462.1	478.6	486.4	503.5	515.3
Conc. 2,6-*cis*	(mol/L)		0.0187	0.0153	0.0131	0.0118	0.0109	0.0105	0.0101	0.0099	0.0095	0.0092
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0035	0.0057	0.0070	0.0078	0.0084	0.0087	0.0089	0.0091	0.0092
ln [*trans* eq/*trans* eq-*trans* t]			0.0093	0.4737	0.9366	1.3739	1.7904	2.2351	2.6313	3.0250	3.3605	4.1263
ln [*cis* t -*cis* eq]			-4.668	-5.119	-5.586	-6.031	-6.447	-6.802	-7.184	-7.558	-8.955	#NUM!
cis + *trans*	(mol/L)		0.0188	0.0189	0.0188	0.0188	0.0188	0.0189	0.0188	0.0188	0.0186	0.0184

Table A.24 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.82 mM trifluoromethanesulphonic acid in nitromethane at 70°C

3-3 (0.74mM Triflic Acid)	time (sec)	0	441	1759	3077	4396	5716	7035	8353	9673	10992
	% 2,6-*trans*	0	0.6	7.5	11.9	15.6	18.6	21.3	23.7	25.8	27.7
area Naphthalene			741.5	743.8	731.6	727.9	732.7	732.7	730.0	728.7	738.6
area 2,6-*cis*			1005.7	952.1	899.8	857.9	834.7	804.9	778.3	755.3	737.2
area 2,6-*trans*			5.6	76.7	121.6	158.0	191.3	218.2	241.8	262.7	282.4
Conc. 2,6-*cis*	(mol/L)		0.0184	0.0174	0.0167	0.0160	0.0155	0.0149	0.0145	0.0141	0.0136
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0014	0.0023	0.0029	0.0035	0.0040	0.0045	0.0049	0.0052
ln [*trans* eq/*trans* eq-*trans* t]			0.0110	0.1622	0.2763	0.3787	0.4767	0.5665	0.6559	0.7414	0.8103
ln [*cis* t -*cis* eq]			-4.6921	-4.8120	-4.8994	-4.9976	-5.0801	-5.1731	-5.2538	-5.3340	-5.4484
cis + *trans*	(mol/L)		0.0185	0.0188	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190	0.0187

3-3 (0.74mM Triflic Acid)	time (sec)	12312	13631	16268	18907	21546	24186	26825	40016	66440	78324
	% 2,6-*trans*	29.4	30.9	33.5	35.7	37.4	38.9	40.2	43.9	46.4	46.8
area Naphthalene		727.7	732.8	737.8	733.7	724.1	733.0	726.9	736.0	725.5	739.7
area 2,6-*cis*		716.7	700.3	676.0	649.0	631.0	615.9	604.0	565.7	539.2	540.2
area 2,6-*trans*		298.3	313.4	340.8	359.7	377.6	392.3	405.6	443.1	467.1	474.6
Conc. 2,6-*cis*	(mol/L)	0.0134	0.0130	0.0124	0.0120	0.0118	0.0114	0.0113	0.0104	0.0101	0.0099
Conc. 2,6-*trans*	(mol/L)	0.0056	0.0058	0.0063	0.0067	0.0071	0.0073	0.0076	0.0082	0.0087	0.0087
ln [*trans* eq/*trans* eq-*trans* t]		0.9047	0.9705	1.1112	1.2448	1.4161	1.5018	1.6626	2.0741	2.7339	2.6854
ln [*cis* t -*cis* eq]		-5.4910	-5.5922	-5.7473	-5.8920	-5.9588	-6.1378	-6.1982	-6.7364	-7.0797	-7.3132
cis + *trans*	(mol/L)	0.0189	0.0188	0.0187	0.0187	0.0189	0.0187	0.0189	0.0186	0.0188	0.0186

Table A.25 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.74 mM trifluoromethanesulphonic acid in nitromethane at 70°C

3-4 (0.90mM Triflic Acid)	time (sec)	0	78	1397	2717	4036	5358	6678	7999	9319	10639	11959
	% 2,6-*trans*	0	0.5	9.3	16.1	21.3	25.4	28.9	31.8	34.2	36.2	37.9
area Naphthalene			782.60	777.60	783.60	783.60	780.50	784.50	779.20	778.60	782.70	786.50
area 2,6-*cis*			1127.80	1021.50	947.80	889.20	836.00	802.70	766.80	738.30	718.50	699.70
area 2,6-*trans*			5.10	105.20	181.30	240.50	285.30	325.60	356.90	383.50	407.90	427.10
Conc. 2,6-*cis*	(mol/L)		0.0196	0.0178	0.0164	0.0154	0.0145	0.0139	0.0134	0.0129	0.0125	0.0121
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0018	0.0031	0.0042	0.0050	0.0056	0.0062	0.0067	0.0071	0.0074
ln [*trans* eq/*trans* eq-*trans* t]			0.0091	0.2076	0.3865	0.5538	0.7062	0.8559	1.0069	1.1472	1.2805	1.3961
ln [*cis* t -*cis* eq]			-4.6184	-4.8112	-5.0020	-5.1657	-5.3299	-5.4741	-5.6095	-5.7521	-5.8907	-6.0405
cis + *trans*	(mol/L)		0.0197	0.0197	0.0196	0.0196	0.0195	0.0195	0.0196	0.0196	0.0195	0.0195

3-4 (0.90mM Triflic Acid)	time (sec)	13280	14600	15920	18560	21200	26480	34393	44946	71337	124083
	% 2,6-*trans*	39.4	40.6	41.8	43.5	44.9	46.7	48.1	49.0	49.7	49.9
area Naphthalene		788.30	791.70	794.20	797.00	802.20	814.50	830.70	831.40	835.80	827.00
area 2,6-*cis*		685.50	672.80	660.60	644.60	632.80	619.10	611.10	601.30	593.40	581.50
area 2,6-*trans*		446.00	460.40	473.60	497.20	515.30	542.10	566.80	577.70	585.40	578.70
Conc. 2,6-*cis*	(mol/L)	0.0118	0.0115	0.0113	0.0110	0.0107	0.0103	0.0100	0.0098	0.0096	0.0095
Conc. 2,6-*trans*	(mol/L)	0.0077	0.0079	0.0081	0.0085	0.0087	0.0090	0.0093	0.0094	0.0095	0.0095
ln [*trans* eq/*trans* eq-*trans* t]		1.5322	1.6387	1.7503	1.9980	2.2078	2.5537	2.9081	3.2912	3.5230	3.4930
ln [*cis* t -*cis* eq]		-6.1619	-6.2982	-6.4411	-6.6590	-6.8963	-7.3836	-8.1481	-9.0213	#NUM!	#NUM!
cis + *trans*	(mol/L)	0.0195	0.0194	0.0194	0.0195	0.0194	0.0194	0.0193	0.0193	0.0192	0.0190

Table A.26 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.9 mM trifluoromethanesulphonic acid in nitromethane at 70°C

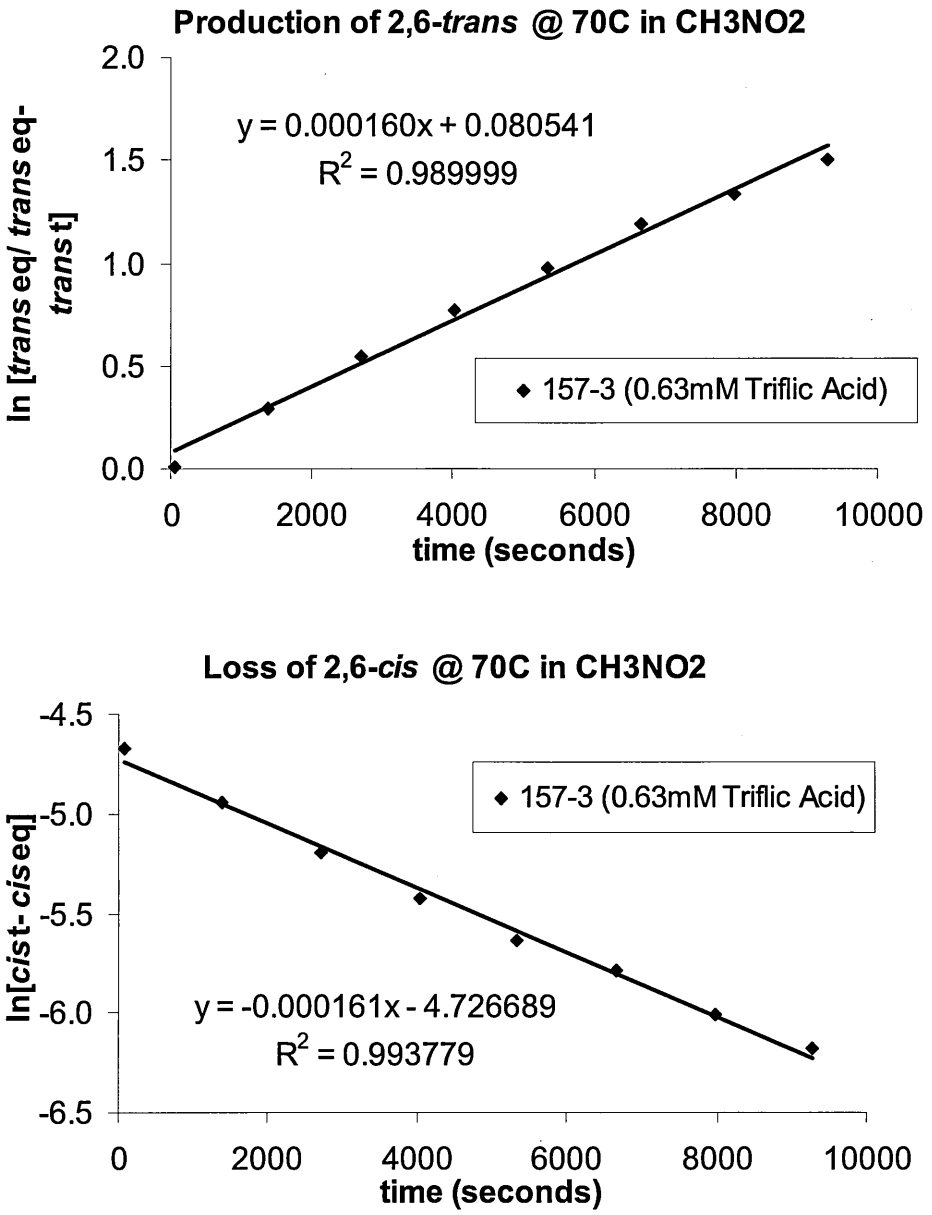


Figure A.23 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.63 mM trifluoromethanesulphonic acid in nitromethane at 70°C

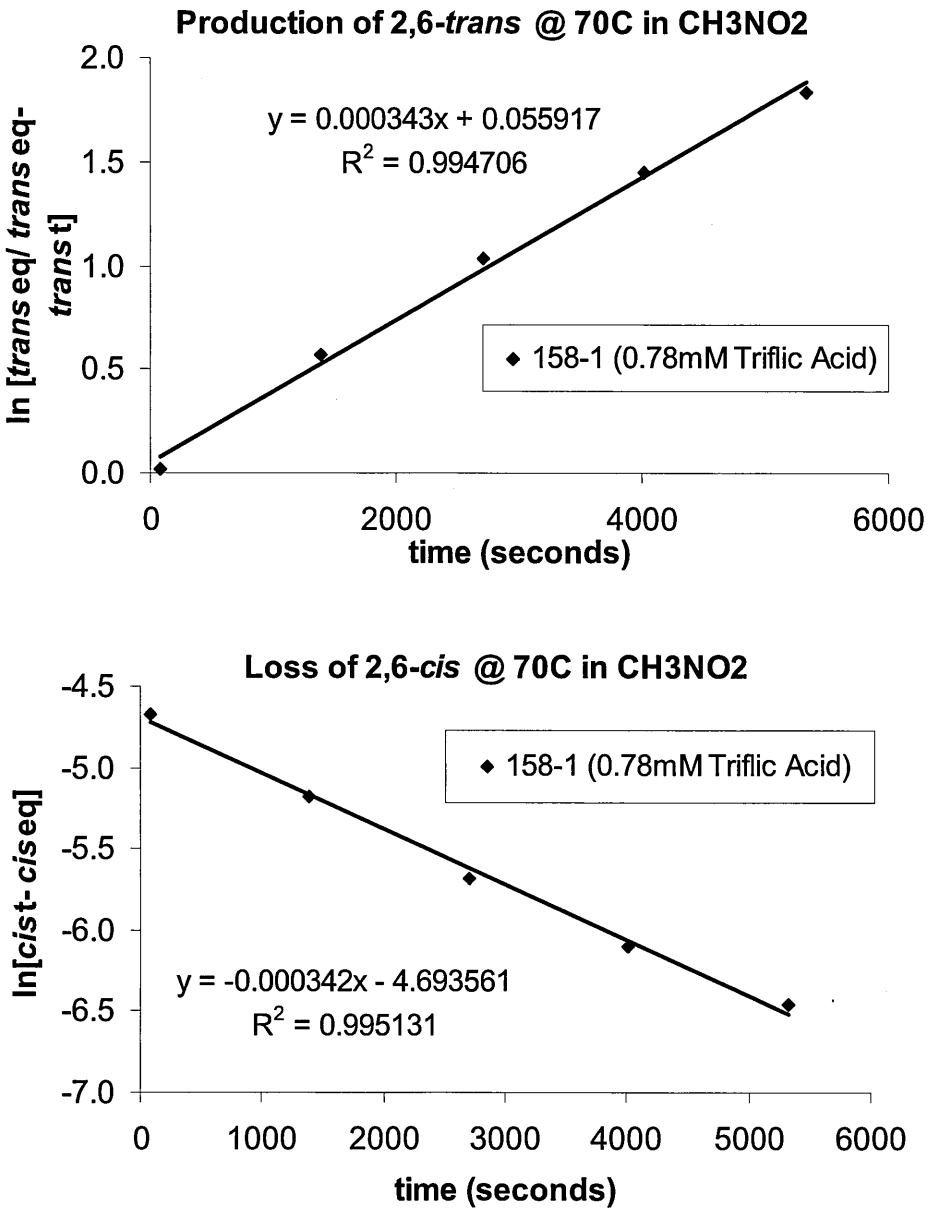
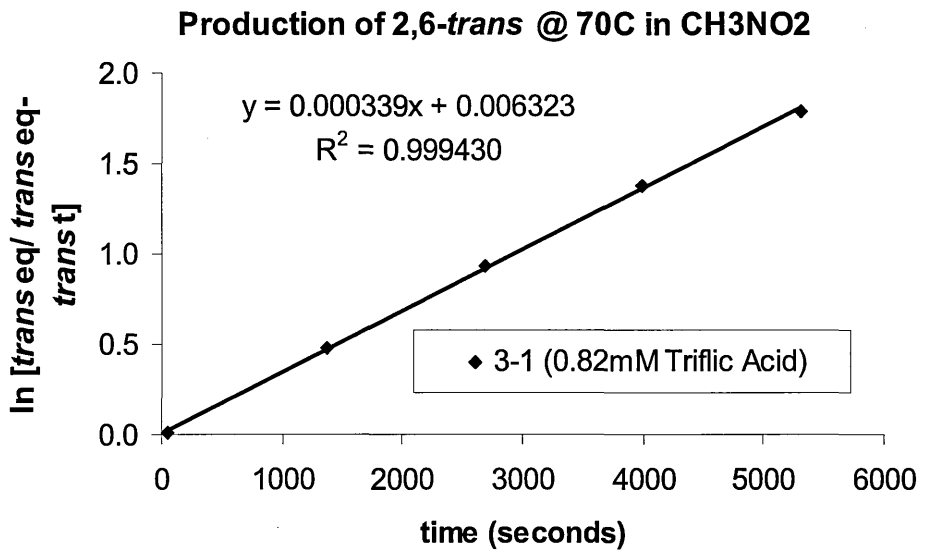


Figure A.24 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.78 mM trifluoromethanesulphonic acid in nitromethane at 70°C



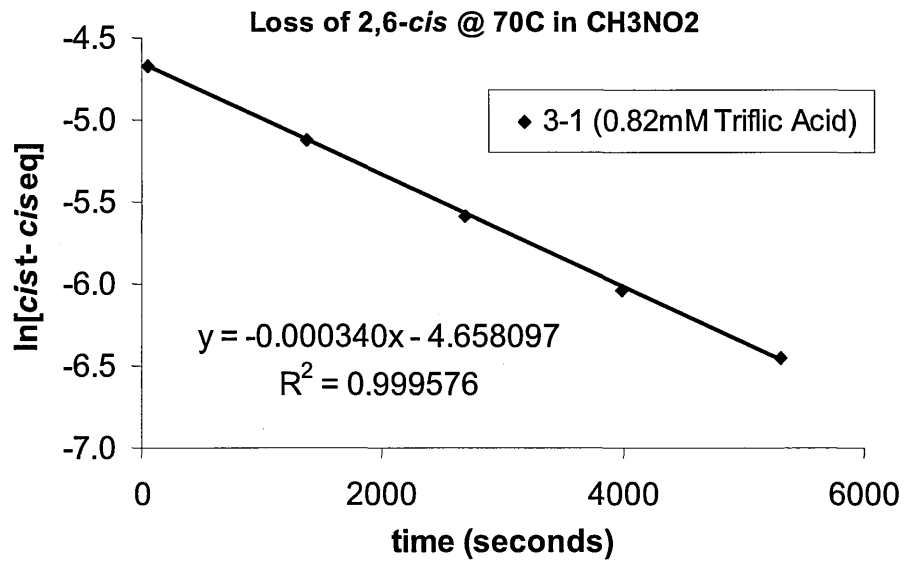
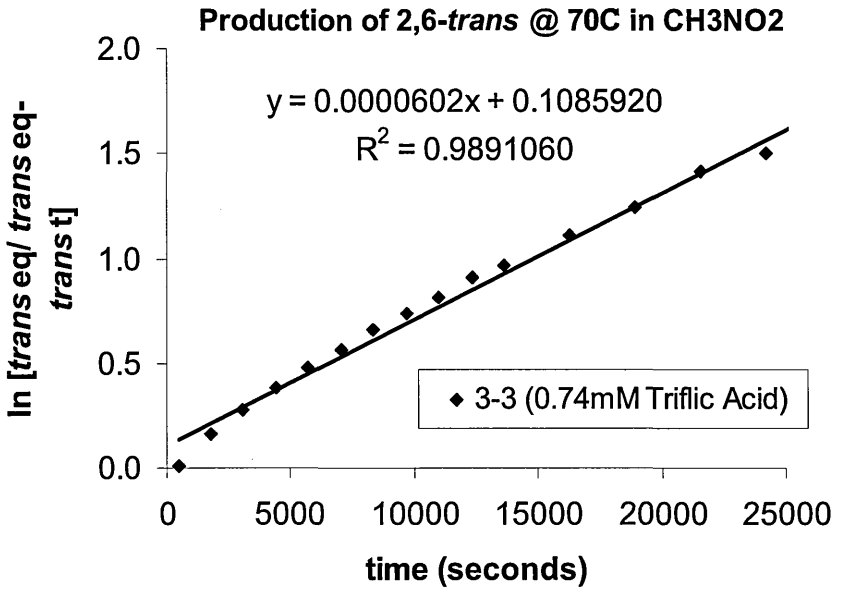


Figure A.25 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.82 mM trifluoromethanesulphonic acid in nitromethane at 70°C



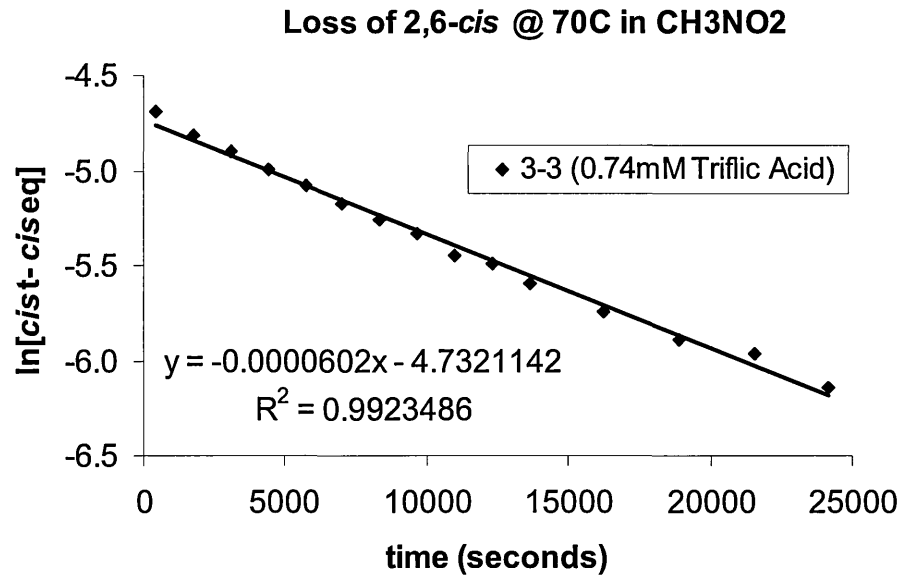
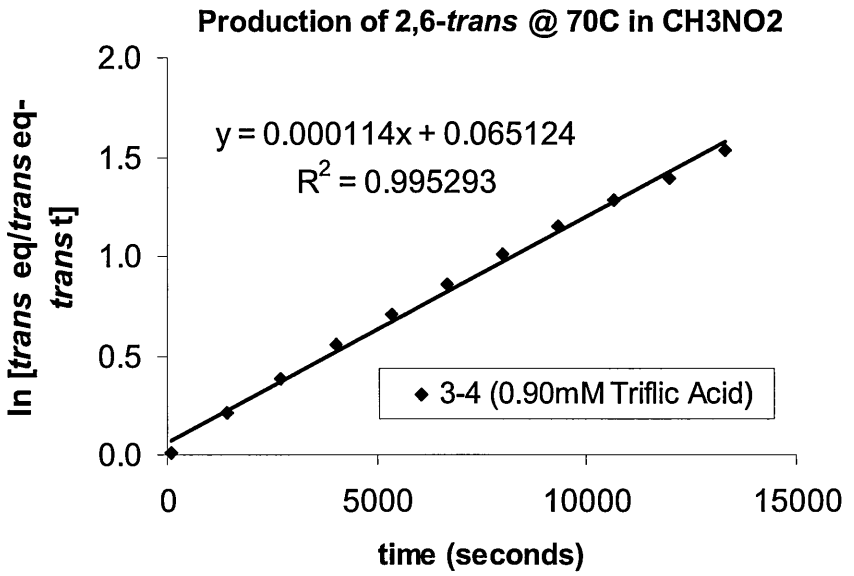


Figure A.26 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.74 mM trifluoromethanesulphonic acid in nitromethane at 70°C



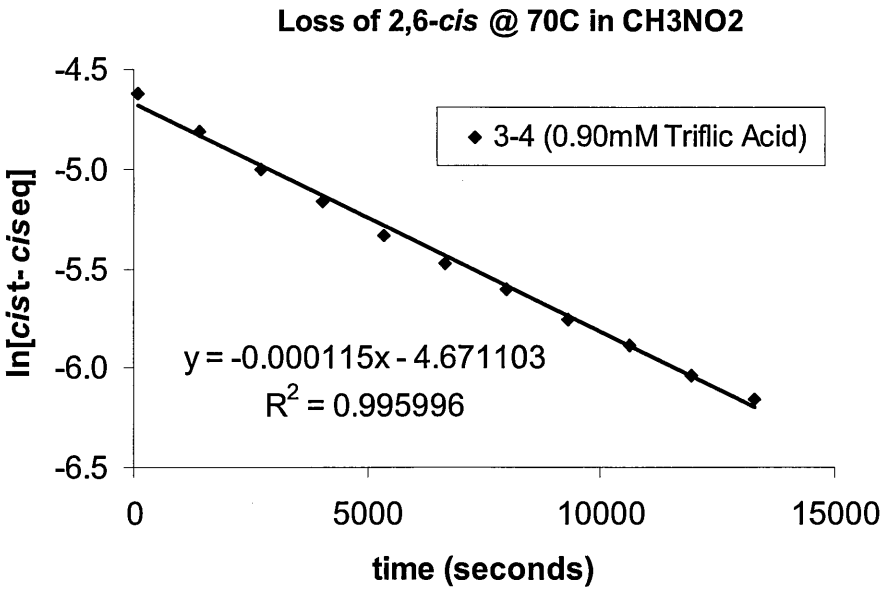


Figure A.27 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.90 mM trifluoromethanesulphonic acid in nitromethane at 70°C

22-1 1.14 mM Triflic Acid	time (sec)	0	154	4089	8028	11967	15907	19846	23786
	% 2,6-*trans*	0	0.4	3.0	5.8	8.2	10.3	12.4	14.2
area Naphthalene			549.90	549.50	541.50	548.70	549.00	547.40	549.10
area 2,6-*cis*			958.80	935.60	901.80	886.70	869.10	845.90	827.70
area 2,6-*trans*			3.90	29.40	55.10	78.90	100.30	119.20	137.50
Conc. 2,6-*cis*	(mol/L)		0.0288	0.0281	0.0275	0.0267	0.0261	0.0255	0.0249
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0009	0.0017	0.0024	0.0030	0.0036	0.0041
ln [*trans* eq/*trans* eq-*trans* t]			0.0081	0.0629	0.1232	0.1789	0.2333	0.2851	0.3358
ln [*cis* t -*cis* eq]			-4.2408	-4.2889	-4.3348	-4.3990	-4.4443	-4.4988	-4.5568
cis + *trans*	(mol/L)		0.0289	0.0290	0.0292	0.0291	0.0292	0.0291	0.0290

22-1 1.14 mM Triflic Acid	time (sec)	27723	35599	43474	51348	63162	78913	126170
	% 2,6-*trans*	16.0	19.0	21.3	23.2	25.3	27.2	30.4
area Naphthalene		552.00	550.30	550.90	547.50	550.80	549.20	549.40
area 2,6-*cis*		815.20	780.70	760.60	740.70	722.40	704.70	673.00
area 2,6-*trans*		155.00	182.70	206.30	223.60	244.30	263.30	293.80
Conc. 2,6-*cis*	(mol/L)	0.0244	0.0234	0.0228	0.0223	0.0217	0.0212	0.0202
Conc. 2,6-*trans*	(mol/L)	0.0046	0.0055	0.0062	0.0067	0.0073	0.0079	0.0088
ln [*trans* eq/*trans* eq-*trans* t]		0.3854	0.4751	0.5561	0.6258	0.7036	0.7898	0.9393
ln [*cis* t -*cis* eq]		-4.6061	-4.7071	-4.7792	-4.8354	-4.9252	-4.9920	-5.1445
cis + *trans*	(mol/L)	0.0290	0.0289	0.0290	0.0291	0.0290	0.0291	0.0291

		7/31/04 2:30pm						
22-2 1.19 mM Triflic Acid + 0.7	time (sec)	0	1464	5402	25097	44786	80226	127482
	% 2,6-*trans*	0	0.3	0.3	0.4	0.5	0.8	1.9
area Naphthalene			551.40	548.30	548.30	549.80	549.00	548.80
area 2,6-*cis*			968.90	960.00	964.30	966.60	963.30	947.40
area 2,6-*trans*			3.10	3.20	3.90	4.70	8.00	18.40
Conc. 2,6-*cis*	(mol/L)		0.0290	0.0289	0.0290	0.0290	0.0290	0.0285
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0001	0.0001	0.0001	0.0002	0.0006
ln [*trans* eq/*trans* eq-*trans* t]			0.0064	0.0066	0.0081	0.0097	0.0166	0.0387
ln [*cis* t -*cis* eq]			-4.2322	-4.2394	-4.2304	-4.2311	-4.2350	-4.2679
cis + *trans*	(mol/L)		0.0291	0.0290	0.0292	0.0292	0.0292	0.0291

Table A.27 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.14 (22-1) or 1.19 (22-2) mM trifluoromethanesulphonic acid with the proton sponge 0.75 mM (22-1) DBMP in nitromethane at 40°C

		7/31/04 2:30pm						
22-3 1.21 mM Triflic Acid + 1.46 mM DBMP	time (sec)	0	2777	6715	26411	46098	81539	128795
	% 2,6-*trans*	0	0.3	0.3	0.3	0.3	0.3	0.3
area Naphthalene			553.80	549.20	550.00	544.80	543.90	548.90
area 2,6-*cis*			965.80	960.80	962.80	957.60	959.80	968.80
area 2,6-*trans*			3.00	3.10	3.20	3.20	3.30	3.20
Conc. 2,6-*cis*	(mol/L)		0.0288	0.0289	0.0289	0.0290	0.0291	0.0292
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
ln [*trans* eq/*trans* eq-*trans* t]			0.0062	0.0065	0.0066	0.0067	0.0069	0.0067
ln [*cis* t -*cis* eq]			-4.2403	-4.2340	-4.2328	-4.2247	-4.2169	-4.2165
cis + *trans*	(mol/L)		0.0289	0.0290	0.0290	0.0291	0.0292	0.0292
		8/2/04 5:10pm						
23-1 2.40 mM Triflic Acid + 0.75 mM DBMP	time (sec)	0	181	1490	2803	4115	5428	6742
	% 2,6-*trans*	0	1.1	18.2	29.6	36.8	41.5	44.5
area Naphthalene			553.80	552.10	378.30	549.60	551.30	548.90
area 2,6-*cis*			958.30	792.40	677.80	608.10	560.10	530.30
area 2,6-*trans*			10.50	176.60	285.00	354.80	397.30	425.50
Conc. 2,6-*cis*	(mol/L)		0.0286	0.0237	0.0296	0.0183	0.0168	0.0160
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0053	0.0124	0.0107	0.0119	0.0128
ln [*trans* eq/*trans* eq-*trans* t]			0.0218	0.4531	1.9527	1.3292	1.7195	2.1452
ln [*cis* t -*cis* eq]			-4.2560	-4.6773	-4.1870	-5.5535	-6.0409	-6.4655
cis + *trans*	(mol/L)		0.0289	0.0290	0.0420	0.0289	0.0287	0.0288

23-1 2.40 mM Triflic Acid + 0.75 mM DBMP	time (sec)	8055	9369	11995	48787
	% 2,6-*trans*	46.5	47.8	49.2	50.4
area Naphthalene		546.40	550.60	549.40	547.10
area 2,6-*cis*		506.10	498.10	482.30	460.10
area 2,6-*trans*		439.70	455.50	467.10	467.70
Conc. 2,6-*cis*	(mol/L)	0.0153	0.0149	0.0145	0.0139
Conc. 2,6-*trans*	(mol/L)	0.0133	0.0137	0.0140	0.0141
ln [*trans* eq/*trans* eq-*trans* t]		2.4840	2.8523	3.4544	3.6388
ln [*cis* t -*cis* eq]		-7.0157	-7.5221	-9.2238	#NUM!
cis + *trans*	(mol/L)	0.0286	0.0286	0.0285	0.0280

Table A.28 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.21 (22-3) or 2.40 (23-1) mM trifluoromethanesulphonic acid with the proton sponge 1.46 (22-3) or 0.75 mM DBMP in nitromethane at 40°C

Appendix B

Data for Interconversion Reactions Catalysed by Methanesulphonic Acid

Appendix B. Data for Interconversion Reactions Catalysed by Methanesulphonic Acid

13-1 Methane sulfonic acid	time (sec)	0	34	1344	2657	3971	5283	6597	9222	11848	14474	17100
	% 2,6-*trans*	0	1.1	3.5	5.8	7.9	10.0	11.9	15.4	18.6	21.5	24.1
area Naphthalene			587.3	578.0	571.1	567.9	569.4	572.2	574.3	577.8	578.8	577.7
area 2,6-*cis*			976.5	940.7	878.0	889.1	866.6	851.6	821.0	796.3	765.9	741.6
area 2,6-*trans*			10.5	34.0	53.9	76.6	96.0	114.9	150.0	182.4	209.9	235.7
Conc. 2,6-*cis*	(mol/L)		0.0226	0.0221	0.0209	0.0213	0.0207	0.0202	0.0194	0.0187	0.0180	0.0174
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0008	0.0013	0.0018	0.0023	0.0027	0.0035	0.0043	0.0049	0.0055
ln [*trans* eq/*trans* eq-*trans* x]			0.0214	0.0720	0.1224	0.1720	0.2215	0.2703	0.3678	0.4640	0.5595	0.6547
ln [*cis-cis* eq]			-4.4907	-4.5379	-4.6211	-4.6295	-4.6848	-4.7345	-4.8310	-4.9254	-5.0256	-5.1174
cis + *trans*	(mol/L)		0.0228	0.0229	0.0222	0.0231	0.0230	0.0229	0.0230	0.0230	0.0229	0.0230
ln [*cis* + *trans*]			-3.7801004	-3.7767	-3.8096	-3.7683	-3.7742	-3.7750	-3.7741	-3.7722	-3.7769	-3.7735

13-1 Methane sulfonic acid	time (sec)	27616	30246	32877	35506	38134	40762	43391	48651	55221	63110	77567
	% 2,6-*trans*	32.3	33.9	35.3	36.7	37.8	38.9	39.9	41.6	43.3	44.9	46.9
area Naphthalene		583.2	574.2	583.8	572.4	579.5	578.9	580.7	578.7	575.9	565.4	567.4
area 2,6-*cis*		656.5	638.0	626.2	606.3	595.7	584.4	577.0	555.5	537.2	515.0	496.7
area 2,6-*trans*		313.5	327.1	341.6	351.0	361.9	371.6	382.9	394.9	409.7	420.0	438.7
Conc. 2,6-*cis*	(mol/L)	0.0153	0.0151	0.0146	0.0144	0.0140	0.0137	0.0135	0.0130	0.0127	0.0124	0.0119
Conc. 2,6-*trans*	(mol/L)	0.0073	0.0077	0.0079	0.0083	0.0085	0.0087	0.0090	0.0093	0.0097	0.0101	0.0105
ln [*trans* eq/*trans* eq-*trans* x]		1.0323	1.1244	1.2144	1.3108	1.3977	1.4886	1.5829	1.7586	1.9798	2.2520	2.7220
ln [*cis-cis* eq]		-5.5119	-5.5935	-5.6973	-5.7849	-5.8838	-5.9753	-6.0687	-6.2509	-6.4709	-6.7374	-7.2105
cis + *trans*	(mol/L)	0.0226	0.0228	0.0225	0.0227	0.0224	0.0224	0.0224	0.0223	0.0223	0.0225	0.0224
ln [*cis* + *trans*]		-3.7905	-3.7800	-3.7938	-3.7850	-3.7970	-3.7976	-3.7966	-3.8031	-3.8020	-3.7962	-3.7993

Table B.1 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 40°C

13-2 Methane sulfonic acid	time (sec)	0	34	1345	2658	3974	5290	7924	10559	13195	15829	18464
	% 2,6-*trans*	0	1.5	3.3	5.0	6.6	8.2	11.2	13.9	16.5	18.9	21.1
area Naphthalene			583.2	574.6	577.6	578.4	584.0	585.2	578.0	576.6	581.7	578.6
area 2,6-*cis*			966.6	948.6	932.7	919.6	907.2	872.5	838.4	809.7	793.2	766.6
area 2,6-*trans*			14.7	32.0	49.0	65.5	81.0	109.7	135.8	160.3	184.7	204.9
Conc. 2,6-*cis*	(mol/L)		0.0225	0.0224	0.0219	0.0216	0.0211	0.0202	0.0197	0.0191	0.0185	0.0180
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0008	0.0012	0.0015	0.0019	0.0025	0.0032	0.0038	0.0043	0.0048
ln [*trans* eq/*trans* eq-*trans* x]			0.0303	0.0672	0.1047	0.1421	0.1783	0.2517	0.3253	0.3993	0.4720	0.5450
ln [*cis-cis* eq]			-4.4983	-4.5211	-4.5627	-4.5980	-4.6407	-4.7222	-4.7916	-4.8675	-4.9409	-5.0151
cis + *trans*	(mol/L)		0.0228	0.0232	0.0231	0.0231	0.0230	0.0228	0.0229	0.0228	0.0228	0.0228
ln [*cis* + *trans*]			-3.7789	-3.7647	-3.7688	-3.7668	-3.7733	-3.7814	-3.7772	-3.7791	-3.7798	-3.7810

13-2 Methane sulfonic acid	time (sec)	26367	29001	31634	34269	36903	39537	43485	47431	51377	56646	60590
	% 2,6-*trans*	26.8	28.5	30.0	31.4	32.7	33.9	35.6	37.1	38.4	39.9	41.0
area Naphthalene		578.9	579.4	581.1	577.6	576.4	576.5	577.1	577.1	575.6	575.2	572.0
area 2,6-*cis*		708.5	696.1	680.9	665.4	646.7	635.5	620.4	607.7	589.4	573.0	560.8
area 2,6-*trans*		259.8	277.1	291.4	304.7	314.4	326.4	342.7	358.0	367.3	381.2	389.1
Conc. 2,6-*cis*	(mol/L)	0.0166	0.0163	0.0159	0.0156	0.0152	0.0150	0.0146	0.0143	0.0139	0.0135	0.0133
Conc. 2,6-*trans*	(mol/L)	0.0061	0.0065	0.0068	0.0072	0.0074	0.0077	0.0081	0.0084	0.0087	0.0090	0.0092
ln [*trans* eq/*trans* eq-*trans* x]		0.7646	0.8375	0.9089	0.9826	1.0545	1.1269	1.2338	1.3412	1.4473	1.5887	1.6927
ln [*cis-cis* eq]		-5.2386	-5.3073	-5.3825	-5.4525	-5.5316	-5.6033	-5.7101	-5.8148	-5.9276	-6.0709	-6.1739
cis + *trans*	(mol/L)	0.0227	0.0228	0.0227	0.0228	0.0226	0.0227	0.0227	0.0227	0.0226	0.0225	0.0226
ln [*cis* + *trans*]		-3.7848	-3.7806	-3.7845	-3.7807	-3.7880	-3.7873	-3.7871	-3.7844	-3.7912	-3.7931	-3.7920

Table B.2 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 23 mM methanesulphonic acid in nitromethane at 40°C

13-3 Methane sulfonic acid	time (sec)	0	89	1401	2713	4026	5339	6655	7972	9288	11920	14551
	% 2,6-*trans*	0	1.1	3.0	5.0	6.9	8.7	10.5	12.1	13.7	16.7	19.4
area Naphthalene			571.3	574.5	574.8	574.5	576.1	575.8	575.5	576.1	576.8	576.6
area 2,6-*cis*			961.1	951.1	931.3	907.9	890.3	873.8	855.0	844.0	816.4	784.4
area 2,6-*trans*			10.7	29.6	49.1	67.3	85.1	102.2	117.6	133.9	163.2	188.5
Conc. 2,6-*cis*	(mol/L)		0.0228	0.0225	0.0220	0.0215	0.0210	0.0206	0.0202	0.0199	0.0192	0.0185
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0007	0.0012	0.0016	0.0020	0.0024	0.0028	0.0032	0.0038	0.0044
ln [*trans* eq/*trans* eq-*trans* x]			0.0222	0.0620	0.1051	0.1479	0.1909	0.2339	0.2756	0.3185	0.4033	0.4877
ln [*cis-cis* eq]			-4.4793	-4.5156	-4.5595	-4.6071	-4.6527	-4.6946	-4.7392	-4.7778	-4.8620	-4.9529
cis + *trans*	(mol/L)		0.0231	0.0232	0.0232	0.0230	0.0230	0.0230	0.0229	0.0230	0.0231	0.0229
ln [*cis* + *trans*]			-3.7680	-3.7645	-3.7653	-3.7701	-3.7727	-3.7715	-3.7745	-3.7701	-3.7696	-3.7761

13-3 Methane sulfonic acid	time (sec)	19814	22445	25075	27706	30336	32966	36908	40851	46117	51385	60704
	% 2,6-*trans*	24.1	26.2	28.1	29.9	31.4	33.0	34.9	36.7	38.7	40.4	42.7
area Naphthalene		577.4	578.4	573.9	575.2	578.0	572.0	570.9	573.9	567.7	568.6	570.5
area 2,6-*cis*		739.8	720.4	698.7	679.7	669.6	645.2	626.8	609.5	585.7	570.0	546.8
area 2,6-*trans*		235.3	256.2	273.5	289.6	307.0	317.1	335.9	352.9	369.2	386.0	408.0
Conc. 2,6-*cis*	(mol/L)	0.0174	0.0169	0.0165	0.0160	0.0157	0.0153	0.0149	0.0144	0.0140	0.0136	0.0130
Conc. 2,6-*trans*	(mol/L)	0.0055	0.0060	0.0065	0.0068	0.0072	0.0075	0.0080	0.0083	0.0088	0.0092	0.0097
ln [*trans* eq/*trans* eq-*trans* x]		0.6553	0.7394	0.8219	0.9043	0.9841	1.0683	1.1876	1.3110	1.4705	1.6312	1.9053
ln [*cis-cis* eq]		-5.1196	-5.2040	-5.2832	-5.3708	-5.4479	-5.5365	-5.6535	-5.7824	-5.9389	-6.1001	-6.3787
cis + *trans*	(mol/L)	0.0229	0.0229	0.0230	0.0229	0.0229	0.0228	0.0229	0.0228	0.0228	0.0228	0.0227
ln [*cis* + *trans*]		-3.7752	-3.7754	-3.7721	-3.7774	-3.7747	-3.7790	-3.7767	-3.7823	-3.7792	-3.7797	-3.7842

Table B.3 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 21 mM methanesulphonic acid in nitromethane at 40°C

14-1 Methane sulfonic acid	time (sec)	0	39	1351	2664	5289	7917	10547	13172	15799	18426	21052
	% 2,6-*trans*	0	1.1	2.8	4.5	7.6	10.5	13.2	15.7	18.1	20.3	22.2
area Naphthalene			579.4	577.9	584.7	583.9	580.8	581.9	585.1	583.2	581.8	584.7
area 2,6-*cis*			972.4	952.8	943.8	912.1	882.2	856.0	834.1	806.1	782.2	767.6
area 2,6-*trans*			10.8	27.6	44.5	75.3	103.3	130.4	155.8	178.4	198.9	219.3
Conc. 2,6-*cis*	(mol/L)		0.0228	0.0224	0.0219	0.0212	0.0206	0.0200	0.0194	0.0188	0.0183	0.0178
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0006	0.0010	0.0018	0.0024	0.0030	0.0036	0.0042	0.0046	0.0051
ln [*trans* eq/*trans* eq-*trans* x]			0.0221	0.0577	0.0940	0.1648	0.2342	0.3056	0.3762	0.4478	0.5173	0.5846
ln [*cis-cis* eq]			-4.4817	-4.5175	-4.5575	-4.6278	-4.6939	-4.7663	-4.8388	-4.9126	-4.9831	-5.0495
cis + *trans*	(mol/L)		0.0230	0.0230	0.0230	0.0230	0.0230	0.0230	0.0230	0.0229	0.0229	0.0229
ln [*cis* + *trans*]			-3.7704	-3.7707	-3.7743	-3.7739	-3.7705	-3.7715	-3.7734	-3.7756	-3.7767	-3.7758

14-1 Methane sulfonic acid	time (sec)	26311	30255	32886	35517	43406	47349	51291	55235	56549
	% 2,6-*trans*	25.8	28.2	29.6	31.0	34.4	35.9	37.2	38.4	38.7
area Naphthalene		583.3	579.2	578.8	576.4	582.1	582.3	574.5	576.2	576.0
area 2,6-*cis*		731.4	704.0	687.1	672.6	640.3	625.4	606.0	595.0	592.2
area 2,6-*trans*		254.4	275.9	289.0	301.6	336.3	350.2	358.7	370.4	374.5
Conc. 2,6-*cis*	(mol/L)	0.0170	0.0165	0.0161	0.0158	0.0149	0.0146	0.0143	0.0140	0.0140
Conc. 2,6-*trans*	(mol/L)	0.0059	0.0065	0.0068	0.0071	0.0078	0.0082	0.0085	0.0087	0.0088
ln [*trans* eq/*trans* eq-*trans* x]		0.7217	0.8230	0.8911	0.9590	1.1583	1.2555	1.3497	1.4452	1.4772
ln [*cis-cis* eq]		-5.1853	-5.2856	-5.3569	-5.4225	-5.6292	-5.7278	-5.8198	-5.9175	-5.9478
cis + *trans*	(mol/L)	0.0229	0.0230	0.0229	0.0230	0.0228	0.0228	0.0228	0.0228	0.0228
ln [*cis* + *trans*]		-3.7745	-3.7734	-3.7766	-3.7744	-3.7818	-3.7832	-3.7809	-3.7831	-3.7815

Table B.4 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 40°C

14-2 Methane sulfonic acid	time (sec)	0	44	1353	2664	3977	5289	6601	7914	9226	10540	11853
	% 2,6-*trans*	0	1.3	5.6	9.6	13.1	16.3	19.3	21.9	24.4	26.6	28.6
area Naphthalene			571.0	565.1	564.0	564.3	561.0	561.6	562.8	560.2	564.7	565.3
area 2,6-*cis*			940.5	905.5	862.5	831.3	797.9	763.4	739.9	714.2	691.8	674.0
area 2,6-*trans*			12.2	54.1	91.5	125.4	155.9	182.2	207.9	230.1	250.4	269.8
Conc. 2,6-*cis*	(mol/L)		0.0224	0.0218	0.0208	0.0200	0.0193	0.0185	0.0179	0.0173	0.0166	0.0162
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0013	0.0022	0.0030	0.0038	0.0044	0.0050	0.0056	0.0060	0.0065
ln [*trans* eq/*trans* eq-*trans* x]			0.0258	0.1191	0.2120	0.3026	0.3939	0.4842	0.5744	0.6644	0.7538	0.8427
ln [*cis*-*cis* eq]			-4.5023	-4.5780	-4.6748	-4.7631	-4.8516	-4.9516	-5.0416	-5.1306	-5.2302	-5.3185
cis + *trans*	(mol/L)		0.0227	0.0231	0.0230	0.0230	0.0231	0.0229	0.0229	0.0229	0.0227	0.0227
ln [*cis* + *trans*]			-3.7873	-3.7697	-3.7736	-3.7713	-3.7685	-3.7782	-3.7780	-3.7771	-3.7873	-3.7867

14-2 Methane sulfonic acid	time (sec)	14477	15789	17104	18418	19732	21046	22360	23674	24986	26299	27613
	% 2,6-*trans*	32.1	33.7	35.1	36.4	37.6	38.6	39.6	40.5	41.3	42.1	42.7
area Naphthalene		562.9	562.4	564.9	565.7	565.6	562.6	565.2	561.1	563.6	561.5	563.3
area 2,6-*cis*		636.2	626.4	612.0	599.1	585.7	574.8	568.0	554.2	548.8	536.3	532.2
area 2,6-*trans*		301.1	317.7	330.7	342.6	353.2	361.6	372.5	377.2	386.5	389.3	397.2
Conc. 2,6-*cis*	(mol/L)	0.0153	0.0151	0.0147	0.0144	0.0141	0.0139	0.0136	0.0134	0.0132	0.0130	0.0128
Conc. 2,6-*trans*	(mol/L)	0.0073	0.0077	0.0079	0.0082	0.0085	0.0087	0.0089	0.0091	0.0093	0.0094	0.0096
ln [*trans* eq/*trans* eq-*trans* x]		1.0214	1.1097	1.2000	1.2900	1.3838	1.4664	1.5558	1.6437	1.7326	1.8191	1.9061
ln [*cis*-*cis* eq]		-5.4999	-5.5801	-5.6763	-5.7687	-5.8654	-5.9453	-6.0349	-6.1253	-6.2145	-6.3077	-6.3938
cis + *trans*	(mol/L)	0.0226	0.0228	0.0227	0.0226	0.0225	0.0226	0.0226	0.0225	0.0225	0.0224	0.0224
ln [*cis* + *trans*]		-3.7893	-3.7812	-3.7871	-3.7896	-3.7924	-3.7898	-3.7900	-3.7924	-3.7927	-3.7994	-3.7985

Table B.5 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 26 mM methanesulphonic acid in nitromethane at 40°C

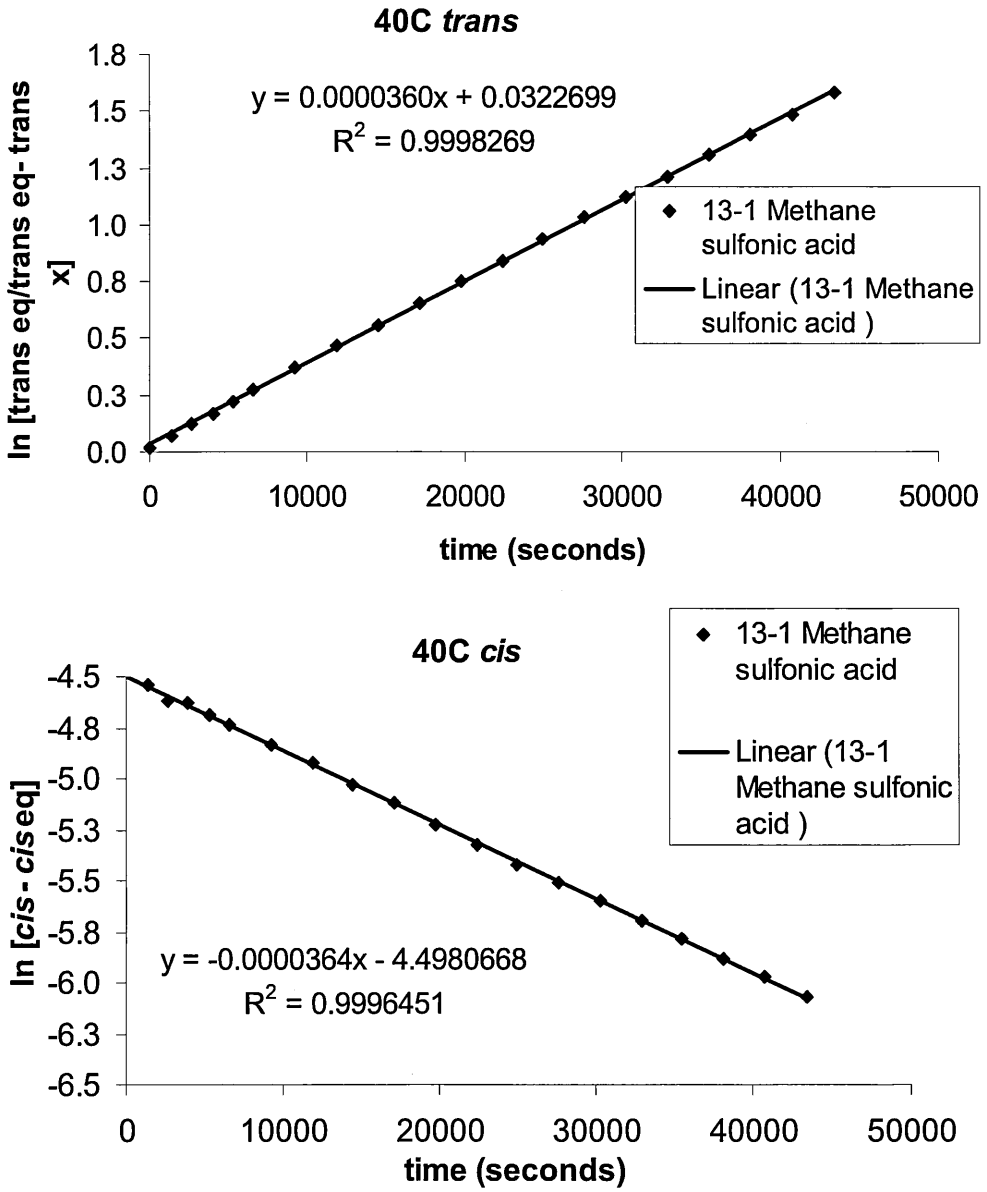


Figure B.1 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 40°C

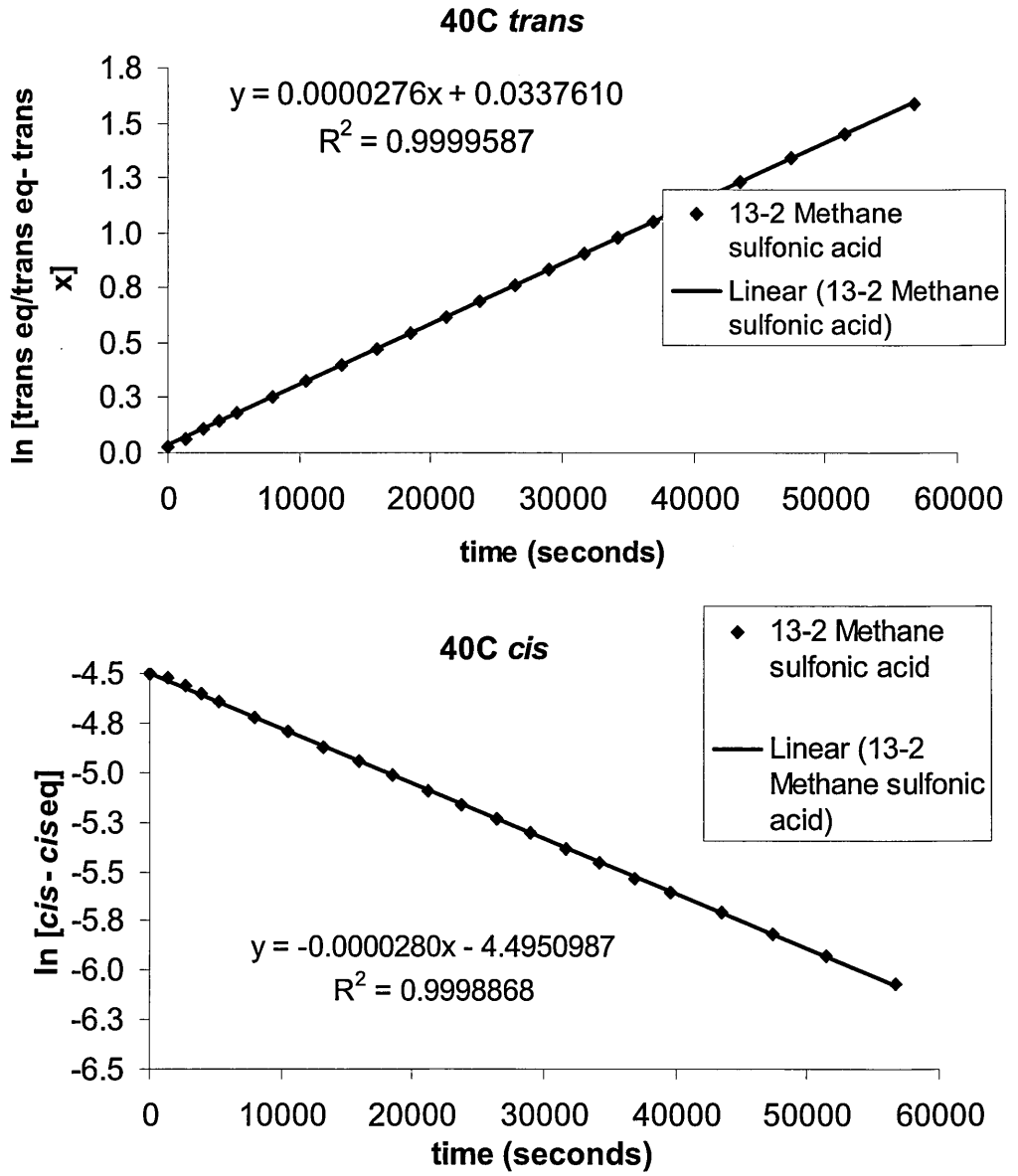


Figure B.2 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 23 mM methanesulphonic acid in nitromethane at 40°C

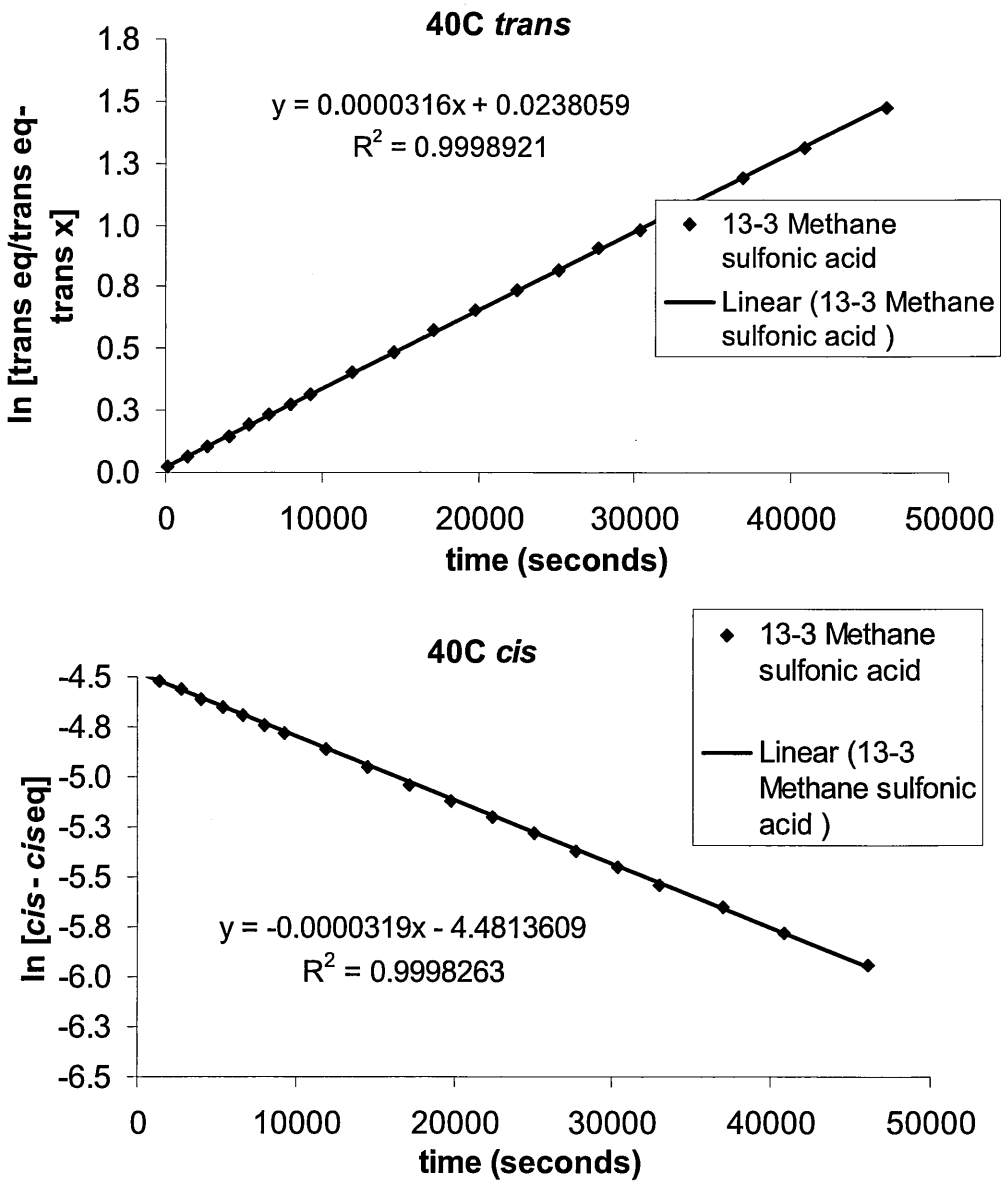


Figure B.3 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 21 mM methanesulphonic acid in nitromethane at 40°C

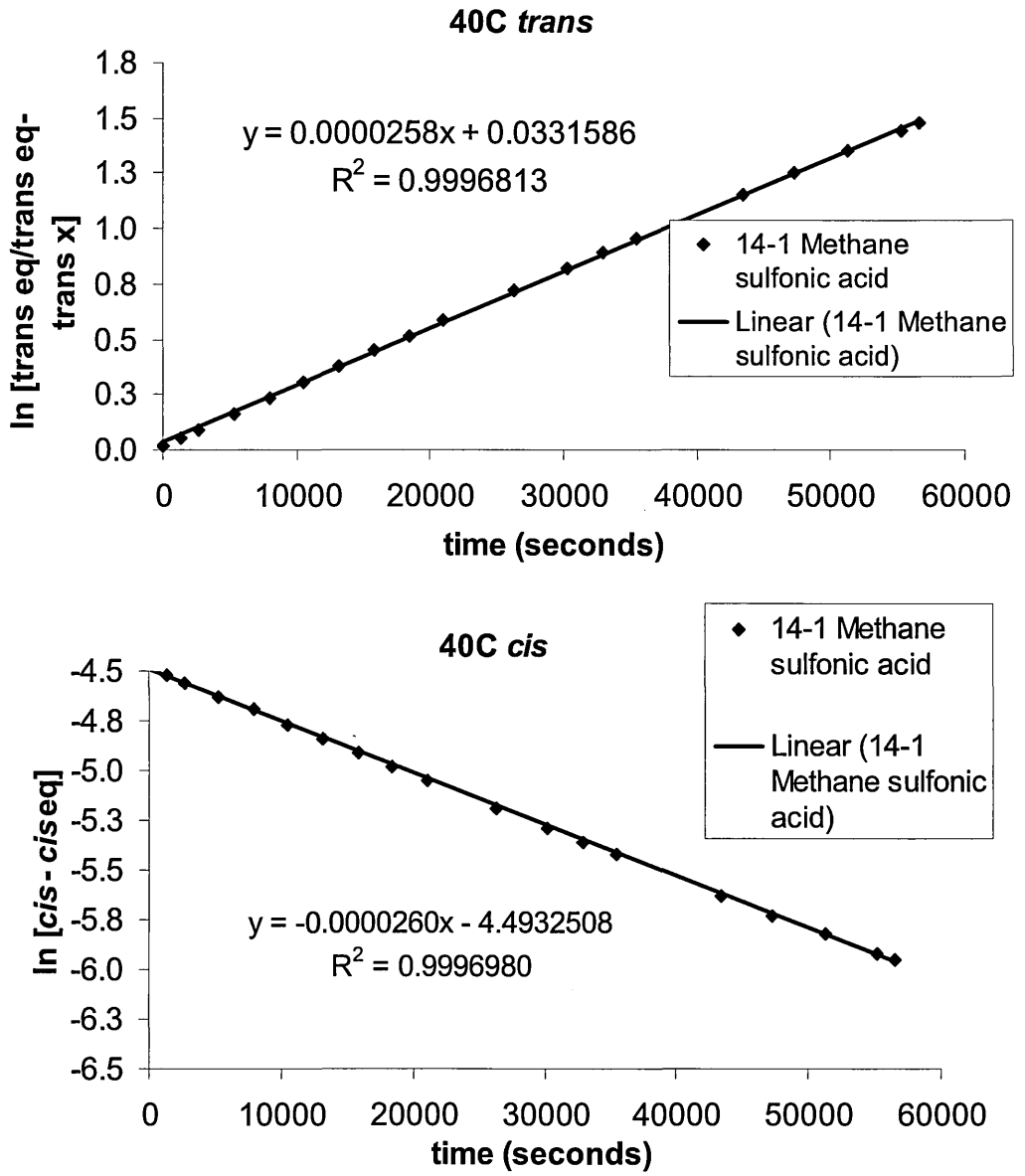


Figure B.4 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 40°C

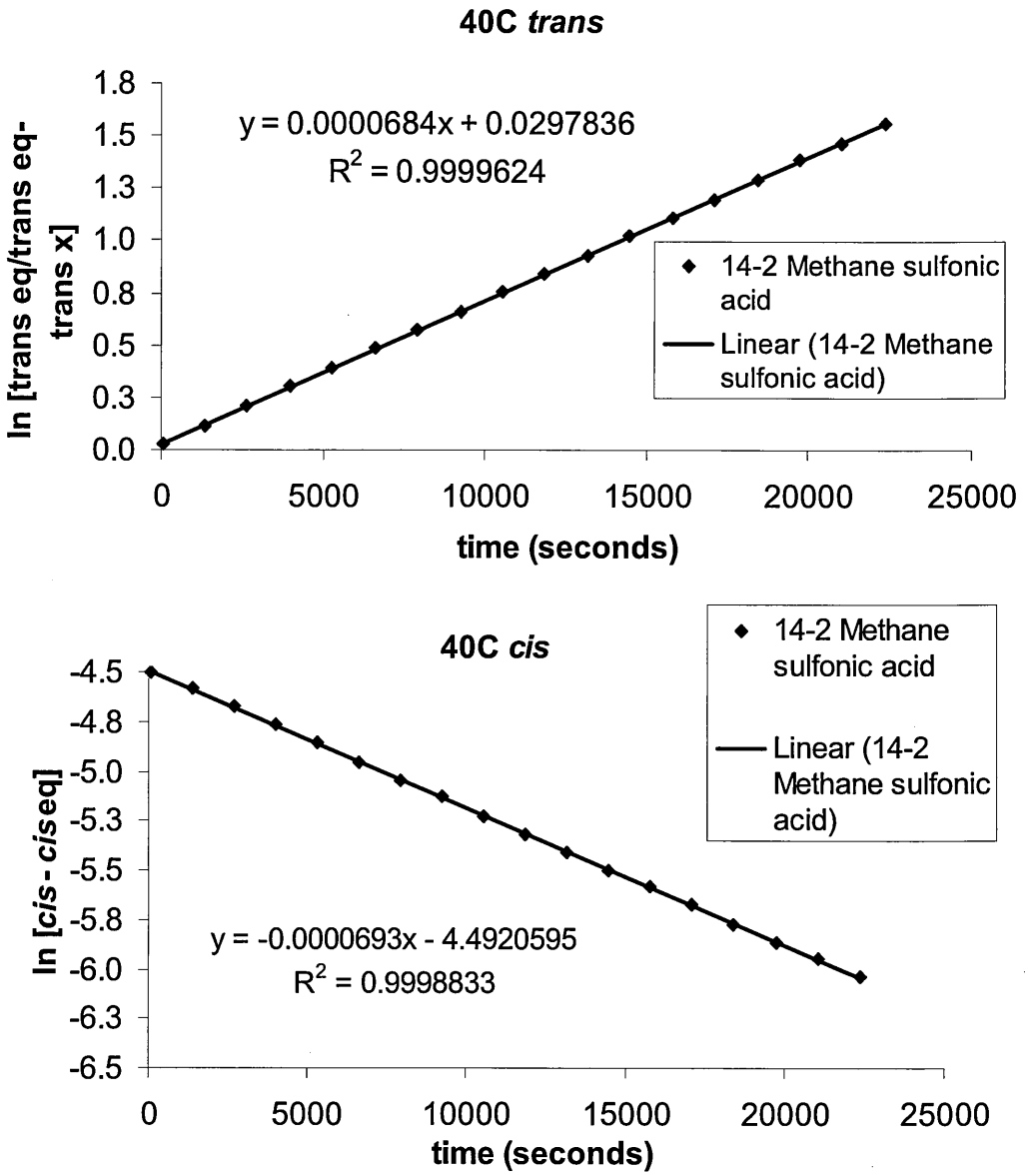


Figure B.5 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 26 mM methanesulphonic acid in nitromethane at 40°C

11-1 Methane sulfonic acid	time (sec)	0	40	2669	5301	7934	10566
	% 2,6-*trans*	0	1.2	6.7	11.5	15.8	19.6
area Naphthalene			540.6	553.4	553.2	554.3	551.9
area 2,6-*cis*			904.4	863.1	817.7	777.7	738.6
area 2,6-*trans*			11.1	62.4	106.5	145.8	179.9
Conc. 2,6-*cis*	(mol/L)		0.0227	0.0212	0.0201	0.0191	0.0182
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0015	0.0026	0.0036	0.0044
ln [*trans* eq/*trans* eq-*trans* x]			0.0244	0.1442	0.2608	0.3776	0.4946
ln [*cis-cis* eq]			-4.4860	-4.6184	-4.7360	-4.8555	-4.9736
cis + *trans*	(mol/L)		0.0230	0.0227	0.0227	0.0226	0.0226
ln [*cis* + *trans*]			-3.7724	-3.7850	-3.7860	-3.7888	-3.7899

11-1 Methane sulfonic acid	time (sec)	13197	15829	18457	21086	23715	26343
	% 2,6-*trans*	22.9	25.9	28.5	30.8	32.9	34.7
area Naphthalene		555.9	555.3	549.5	555.0	560.7	557.3
area 2,6-*cis*		713.0	683.0	650.1	635.7	622.7	600.0
area 2,6-*trans*		211.6	238.6	259.2	283.3	304.8	319.0
Conc. 2,6-*cis*	(mol/L)	0.0174	0.0167	0.0161	0.0156	0.0151	0.0146
Conc. 2,6-*trans*	(mol/L)	0.0052	0.0058	0.0064	0.0069	0.0074	0.0078
ln [*trans* eq/*trans* eq-*trans* x]		0.6086	0.7251	0.8390	0.9521	1.0631	1.1759
ln [*cis-cis* eq]		-5.0882	-5.2069	-5.3237	-5.4362	-5.5482	-5.6641
cis + *trans*	(mol/L)	0.0226	0.0225	0.0225	0.0225	0.0225	0.0224
ln [*cis* + *trans*]		-3.7905	-3.7926	-3.7956	-3.7949	-3.7959	-3.7991

Table B.6 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 50°C

11-2 Methane sulfonic acid	time (sec)	0	1353	3985	6617	9251	11882
	% 2,6-*trans*	0	2.8	6.4	9.8	12.9	15.6
area Naphthalene			556.6	567.3	565.3	563.9	563.8
area 2,6-*cis*			915.6	891.6	851.5	822.6	796.4
area 2,6-*trans*			26.7	61.0	92.5	121.3	147.5
Conc. 2,6-*cis*	(mol/L)		0.0223	0.0213	0.0205	0.0198	0.0192
Conc. 2,6-*trans*	(mol/L)		0.0007	0.0015	0.0022	0.0029	0.0036
ln [*trans* eq/*trans* eq-*trans* x]			0.0581	0.1365	0.2172	0.2957	0.3729
ln [*cis*-*cis* eq]			-4.5200	-4.6065	-4.6928	-4.7690	-4.8460
cis + *trans*	(mol/L)		0.0230	0.0228	0.0227	0.0227	0.0227
ln [*cis* + *trans*]			-3.773	-3.781	-3.786	-3.784	-3.784

11-2 Methane sulfonic acid	time (sec)	14513	17143	19772	22401	25029	27657
	% 2,6-*trans*	18.2	20.5	22.7	24.7	26.6	28.3
area Naphthalene		566.7	566.1	565.4	570.3	570.0	573.5
area 2,6-*cis*		776.2	751.0	727.6	715.6	697.0	683.1
area 2,6-*trans*		172.2	194.2	214.1	234.4	252.0	269.0
Conc. 2,6-*cis*	(mol/L)	0.0186	0.0180	0.0175	0.0170	0.0166	0.0162
Conc. 2,6-*trans*	(mol/L)	0.0041	0.0047	0.0051	0.0056	0.0060	0.0064
ln [*trans* eq/*trans* eq-*trans* x]		0.4489	0.5264	0.6031	0.6763	0.7528	0.8274
ln [*cis*-*cis* eq]		-4.9224	-5.0022	-5.0814	-5.1544	-5.2314	-5.3089
cis + *trans*	(mol/L)	0.0227	0.0227	0.0226	0.0226	0.0226	0.0225
ln [*cis* + *trans*]		-3.784	-3.787	-3.789	-3.789	-3.789	-3.792

Table B.7 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 22 mM methanesulphonic acid in nitromethane at 50°C

11-3 Methane sulfonic acid	time (sec)	0	3024	4337	5649	6963	8278	9592	10906	12222	13537	14853
	% 2,6-*trans*	0	7.9	10.4	12.8	15.1	17.2	19.2	21.1	22.8	24.5	26.0
area Naphthalene			556.2	562.6	563.7	560.2	562.9	562.7	559.5	559.9	560.6	592.8
area 2,6-*cis*			861.0	841.5	817.6	794.1	776.3	756.5	734.5	719.9	702.8	726.7
area 2,6-*trans*			74.1	98.0	120.5	140.8	161.6	179.6	196.1	213.1	228.0	255.2
Conc. 2,6-*cis*	(mol/L)		0.0210	0.0203	0.0197	0.0192	0.0187	0.0183	0.0178	0.0175	0.0170	0.0166
Conc. 2,6-*trans*	(mol/L)		0.0018	0.0024	0.0029	0.0034	0.0039	0.0043	0.0048	0.0052	0.0055	0.0058
ln [*trans* eq/*trans* eq-*trans* x]			0.1718	0.2329	0.2956	0.3567	0.4204	0.4816	0.5443	0.6069	0.6693	0.7293
ln [*cis-cis* eq]			-4.6407	-4.7085	-4.7746	-4.8329	-4.8983	-4.9610	-5.0239	-5.0847	-5.1507	-5.2130
cis + *trans*	(mol/L)		0.0228	0.0227	0.0226	0.0227	0.0226	0.0226	0.0226	0.0226	0.0225	0.0225
ln [*cis* + *trans*]			-3.7797	-3.7865	-3.7899	-3.7871	-3.7887	-3.7903	-3.7904	-3.7886	-3.7922	-3.7946

11-3 Methane sulfonic acid	time (sec)	18801	21433	24065	26698	29329	31960	34589	47746	60922	74074	87205
	% 2,6-*trans*	30.0	32.3	34.3	36.1	37.7	39.1	40.2	44.6	47.0	48.3	49.1
area Naphthalene		559.9	561.2	558.9	558.4	560.7	557.3	556.4	555.6	556.5	558.7	554.4
area 2,6-*cis*		650.2	629.7	607.7	591.7	576.9	559.9	546.6	504.0	479.5	466.7	452.1
area 2,6-*trans*		278.5	300.0	317.8	334.5	348.5	359.3	367.9	405.4	425.1	436.3	436.0
Conc. 2,6-*cis*	(mol/L)	0.0158	0.0152	0.0148	0.0144	0.0140	0.0136	0.0133	0.0123	0.0117	0.0113	0.0111
Conc. 2,6-*trans*	(mol/L)	0.0068	0.0073	0.0077	0.0081	0.0084	0.0088	0.0090	0.0099	0.0104	0.0106	0.0107
ln [*trans* eq/*trans* eq-*trans* x]		0.9097	1.0295	1.1521	1.2709	1.3870	1.5080	1.6164	2.1895	2.7507	3.2830	3.8149
ln [*cis-cis* eq]		-5.3921	-5.5131	-5.6361	-5.7533	-5.8744	-5.9960	-6.1079	-6.6851	-7.2533	-7.7913	-8.3321
cis + *trans*	(mol/L)	0.0225	0.0225	0.0225	0.0225	0.0224	0.0224	0.0223	0.0222	0.0221	0.0219	0.0218
ln [*cis* + *trans*]		-3.7932	-3.7945	-3.7949	-3.7932	-3.7982	-3.7988	-3.8023	-3.8065	-3.8134	-3.8191	-3.8280

Table B.8 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 50°C

12-1 Methane sulfonic acid	time (sec)	0	64	1374	2686	4000	5314	6628	7941	9253	10566
	% 2,6-*trans*	0	1.0	5.4	9.6	13.2	16.6	19.7	22.5	24.9	27.2
area Naphthalene			573.6	567.7	558.0	560.8	559.0	558.0	559.7	558.4	555.2
area 2,6-*cis*			949.2	900.8	860.0	826.3	788.3	758.3	733.9	709.1	680.6
area 2,6-*trans*			9.4	51.3	90.9	125.6	157.2	186.1	212.5	235.5	254.0
Conc. 2,6-*cis*	(mol/L)		0.0225	0.0215	0.0209	0.0200	0.0191	0.0185	0.0178	0.0172	0.0166
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0012	0.0022	0.0030	0.0038	0.0045	0.0052	0.0057	0.0062
ln [*trans* eq/*trans* eq-*trans* x]			0.0197	0.1135	0.2112	0.3050	0.4023	0.4985	0.5929	0.6864	0.7795
ln [*cis-cis* eq]			-4.4946	-4.5849	-4.6666	-4.7642	-4.8651	-4.9607	-5.0560	-5.1491	-5.2471
cis + *trans*	(mol/L)		0.0227	0.0228	0.0231	0.0230	0.0230	0.0230	0.0230	0.0230	0.0229
ln [*cis* + *trans*]			-3.7857	-3.7822	-3.7662	-3.7701	-3.7737	-3.7730	-3.7740	-3.7735	-3.7784

12-1 Methane sulfonic acid	time (sec)	11880	13194	14509	15825	17138	18453	19768	22398	31597
	% 2,6-*trans*	29.2	31.1	32.8	34.4	35.8	37.0	38.1	40.1	44.9
area Naphthalene		558.6	556.6	557.4	557.1	558.1	557.0	556.4	558.1	562.7
area 2,6-*cis*		665.5	646.6	629.2	615.8	600.4	589.5	577.6	557.3	514.2
area 2,6-*trans*		275.0	292.0	307.1	322.4	334.3	345.8	356.1	373.7	418.6
Conc. 2,6-*cis*	(mol/L)	0.0162	0.0158	0.0153	0.0150	0.0146	0.0144	0.0141	0.0136	0.0124
Conc. 2,6-*trans*	(mol/L)	0.0067	0.0071	0.0075	0.0079	0.0081	0.0084	0.0087	0.0091	0.0101
ln [*trans* eq/*trans* eq-*trans* x]		0.8734	0.9669	1.0595	1.1537	1.2464	1.3337	1.4260	1.6074	2.2437
ln [*cis-cis* eq]		-5.3408	-5.4327	-5.5292	-5.6209	-5.7191	-5.8038	-5.8967	-6.0841	-6.7267
cis + *trans*	(mol/L)	0.0229	0.0229	0.0228	0.0229	0.0227	0.0228	0.0228	0.0227	0.0225
ln [*cis* + *trans*]		-3.7783	-3.7767	-3.7806	-3.7780	-3.7835	-3.7809	-3.7816	-3.7875	-3.7938

Table B.9 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 27 mM methanesulphonic acid in nitromethane at 50°C

12-2 Methane sulfonic acid	time (sec)	0	41	1352	2665	3979	5292	6606	7920	9235	10549	11865
	% 2,6-*trans*	0	0.9	3.0	5.2	7.2	9.0	10.9	12.6	14.2	15.8	17.3
area Naphthalene			560.6	554.0	559.5	563.6	564.8	556.6	562.2	567.2	565.5	561.5
area 2,6-*cis*			948.4	915.7	904.9	884.6	873.5	846.7	839.3	815.2	804.3	789.9
area 2,6-*trans*			8.9	28.8	49.3	68.3	86.7	103.2	121.0	135.3	150.7	164.9
Conc. 2,6-*cis*	(mol/L)		0.0230	0.0224	0.0220	0.0213	0.0210	0.0207	0.0203	0.0195	0.0193	0.0191
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0007	0.0012	0.0016	0.0021	0.0025	0.0029	0.0032	0.0036	0.0040
ln [*trans* eq/*trans* eq-*trans* x]			0.0187	0.0627	0.1086	0.1541	0.1983	0.2439	0.2890	0.3335	0.3774	0.4217
ln [*cis-cis* eq]			-4.4720	-4.5176	-4.5632	-4.6173	-4.6560	-4.6978	-4.7420	-4.8056	-4.8418	-4.8791
cis + *trans*	(mol/L)		0.0232	0.0232	0.0232	0.0230	0.0231	0.0232	0.0232	0.0228	0.0229	0.0231
ln [*cis* + *trans*]			-3.7641	-3.7657	-3.7654	-3.7741	-3.7686	-3.7647	-3.7638	-3.7830	-3.7752	-3.7683

12-2 Methane sulfonic acid	time (sec)	18441	21069	23699	26327	28957	31588	35532	39476	43418	47370	51324
	% 2,6-*trans*	23.7	25.9	27.8	29.6	31.3	32.8	34.8	36.7	38.2	39.6	40.8
area Naphthalene		567.8	564.8	563.1	559.8	562.2	556.1	555.3	560.5	561.2	556.6	555.8
area 2,6-*cis*		726.9	700.0	687.6	666.3	649.2	632.4	607.1	589.6	574.9	560.1	548.5
area 2,6-*trans*		225.9	244.7	265.3	280.7	296.1	308.6	324.6	341.5	355.3	367.3	377.7
Conc. 2,6-*cis*	(mol/L)	0.0174	0.0168	0.0166	0.0162	0.0157	0.0154	0.0148	0.0143	0.0139	0.0137	0.0134
Conc. 2,6-*trans*	(mol/L)	0.0054	0.0059	0.0064	0.0068	0.0072	0.0075	0.0079	0.0083	0.0086	0.0090	0.0092
ln [*trans* eq/*trans* eq-*trans* x]		0.6392	0.7256	0.8088	0.8927	0.9781	1.0593	1.1842	1.3116	1.4308	1.5557	1.6731
ln [*cis-cis* eq]		-5.1100	-5.1996	-5.2711	-5.3554	-5.4468	-5.5216	-5.6551	-5.7925	-5.9138	-6.0335	-6.1508
cis + *trans*	(mol/L)	0.0228	0.0227	0.0230	0.0230	0.0228	0.0230	0.0228	0.0226	0.0225	0.0226	0.0226
ln [*cis* + *trans*]		-3.7816	-3.7848	-3.7732	-3.7735	-3.7796	-3.7732	-3.7817	-3.7917	-3.7939	-3.7887	-3.7886

Table B.10 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 50°C

12-3 Methane sulfonic acid	time (sec)	0	25	1336	2648	5274	7905	11849	15795	19738	23682
	% 2,6-*trans*	0	0.9	2.2	3.6	6.3	8.9	12.4	15.6	18.6	21.1
area Naphthalene			569.8	625.3	569.1	570.2	569.3	569.7	569.0	572.4	574.9
area 2,6-*cis*			955.4	1025.6	933.6	910.7	879.7	847.5	811.4	788.0	765.4
area 2,6-*trans*			8.4	23.4	34.8	61.6	86.0	120.5	150.5	179.6	205.1
Conc. 2,6-*cis*	(mol/L)		0.0228	0.0223	0.0223	0.0217	0.0210	0.0202	0.0194	0.0187	0.0181
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0005	0.0008	0.0015	0.0021	0.0029	0.0036	0.0043	0.0048
ln [*trans* eq/*trans* eq-*trans* x]			0.0175	0.0455	0.0743	0.1349	0.1953	0.2850	0.3735	0.4616	0.5464
ln [*cis*-*cis* eq]			-4.4803	-4.5165	-4.5311	-4.5896	-4.6552	-4.7433	-4.8369	-4.9250	-5.0112
cis + *trans*	(mol/L)		0.0230	0.0228	0.0231	0.0232	0.0230	0.0231	0.0230	0.0230	0.0229
ln [*cis* + *trans*]			-3.7736	-3.7819	-3.7676	-3.7656	-3.7708	-3.7691	-3.7742	-3.7743	-3.7756

12-3 Methane sulfonic acid	time (sec)	27626	31571	35515	39459	43404	47347	51295	56568	63144	69715
	% 2,6-*trans*	23.5	25.7	27.7	29.5	31.1	32.6	34.0	35.6	37.4	39.0
area Naphthalene		570.1	591.7	570.4	569.7	574.9	568.0	576.5	566.4	571.3	573.6
area 2,6-*cis*		734.0	734.8	691.1	675.8	658.6	642.6	636.2	611.6	595.2	582.1
area 2,6-*trans*		226.0	254.5	264.7	282.6	297.9	310.8	327.4	338.2	356.3	372.9
Conc. 2,6-*cis*	(mol/L)	0.0175	0.0169	0.0165	0.0161	0.0156	0.0154	0.0150	0.0147	0.0141	0.0138
Conc. 2,6-*trans*	(mol/L)	0.0054	0.0058	0.0063	0.0067	0.0070	0.0074	0.0077	0.0081	0.0085	0.0088
ln [*trans* eq/*trans* eq-*trans* x]		0.6329	0.7184	0.8022	0.8852	0.9687	1.0481	1.1296	1.2355	1.3702	1.5043
ln [*cis*-*cis* eq]		-5.1002	-5.1928	-5.2744	-5.3535	-5.4480	-5.5185	-5.6043	-5.7069	-5.8484	-5.9829
cis + *trans*	(mol/L)	0.0229	0.0227	0.0228	0.0228	0.0226	0.0228	0.0227	0.0228	0.0226	0.0226
ln [*cis* + *trans*]		-3.7781	-3.7852	-3.7830	-3.7791	-3.7901	-3.7813	-3.7855	-3.7823	-3.7891	-3.7895

Table B.11 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 16 mM methanesulphonic acid in nitromethane at 50°C

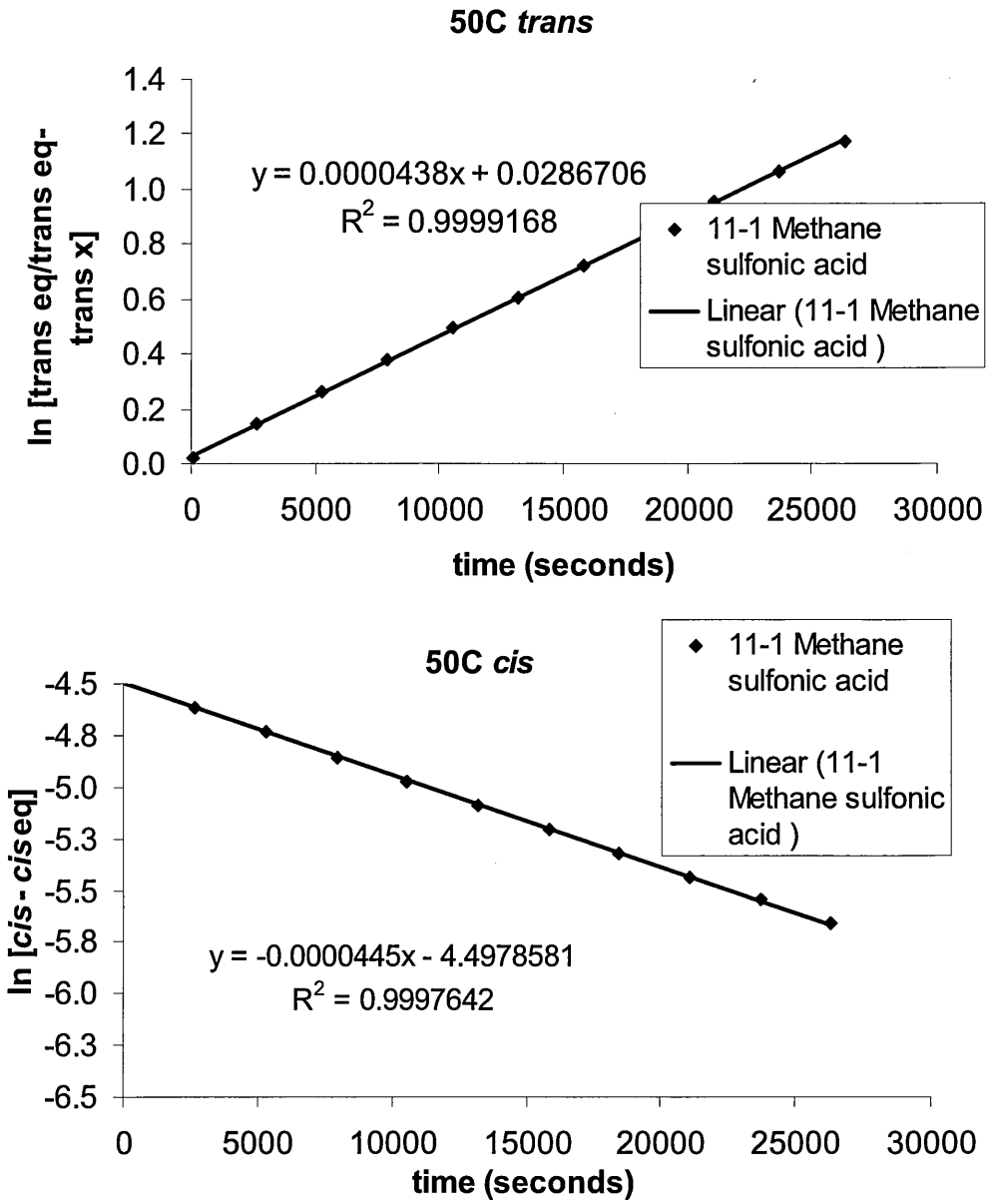


Figure B.6 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 50°C

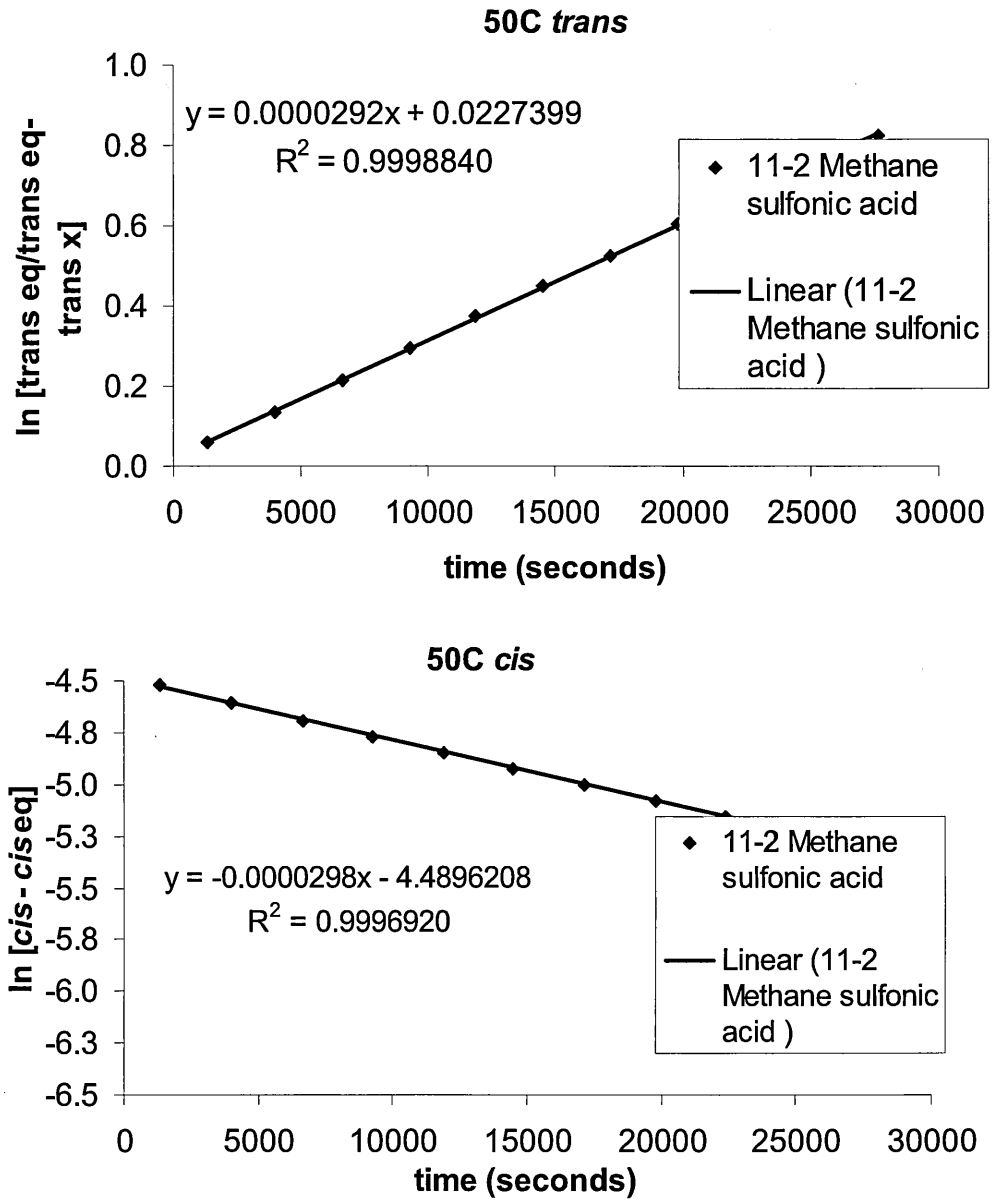


Figure B.7 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 22 mM methanesulphonic acid in nitromethane at 50°C

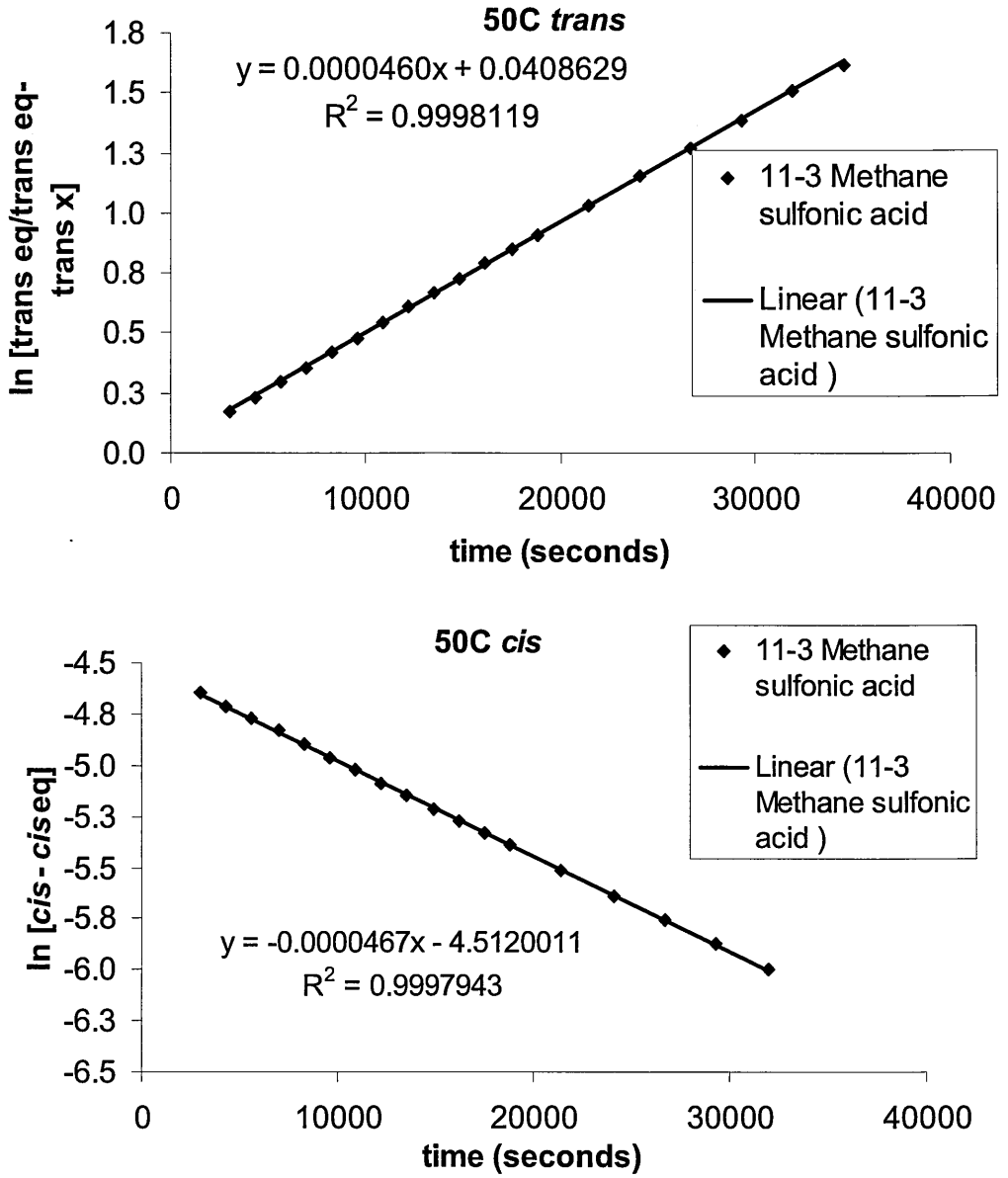


Figure B.8 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 50°C

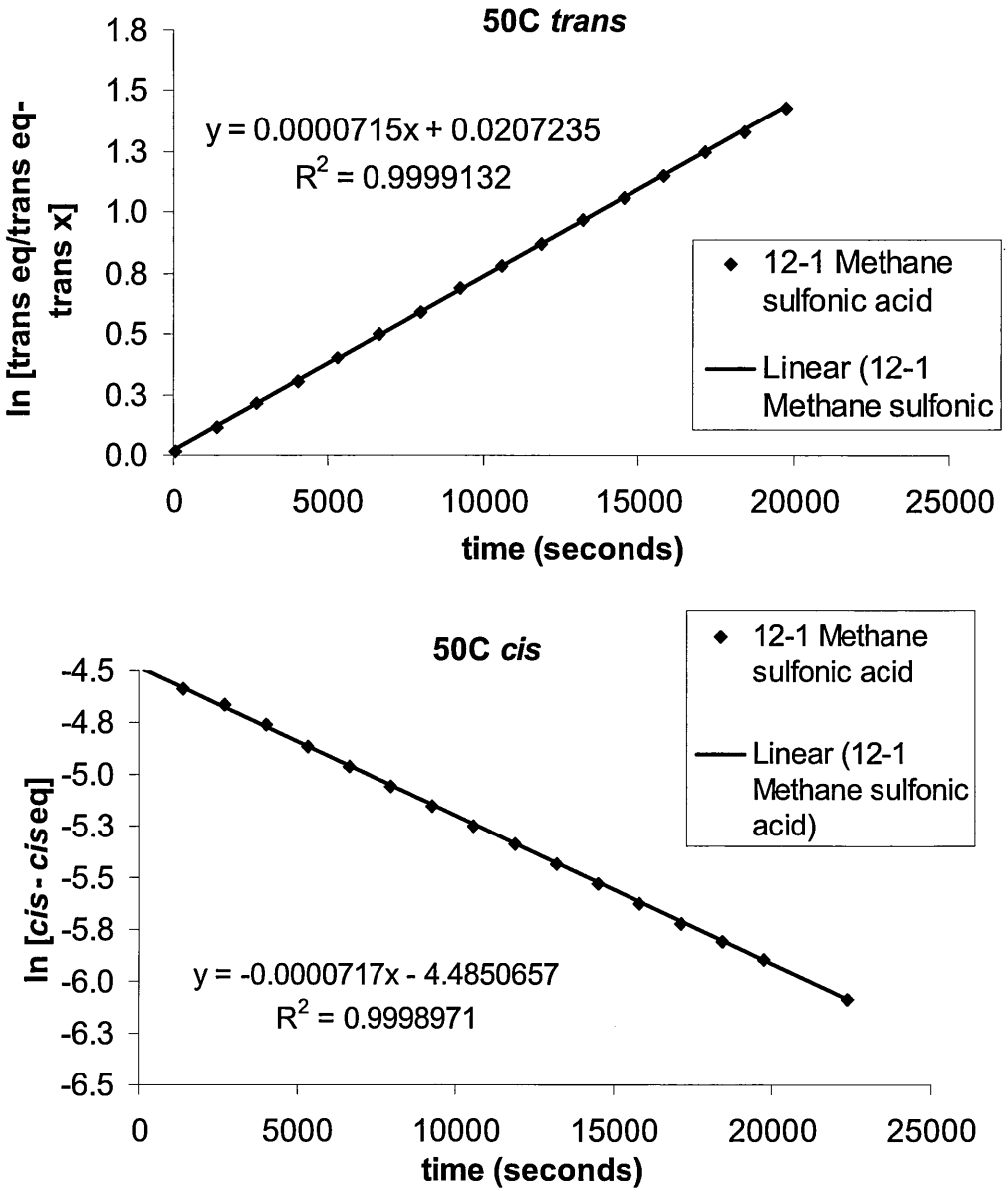


Figure B.9 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 27 mM methanesulphonic acid in nitromethane at 50°C

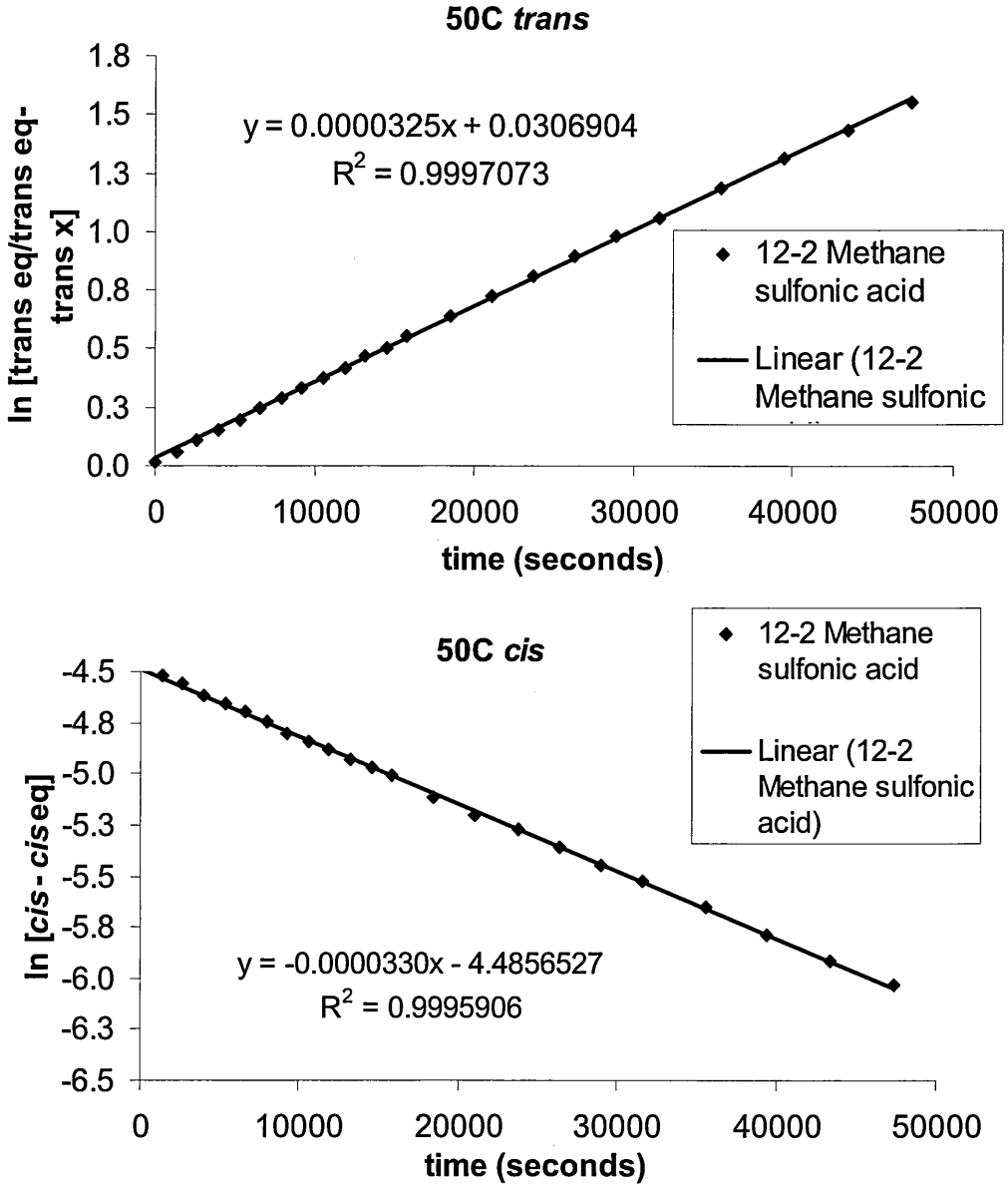


Figure B.10 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 50°C

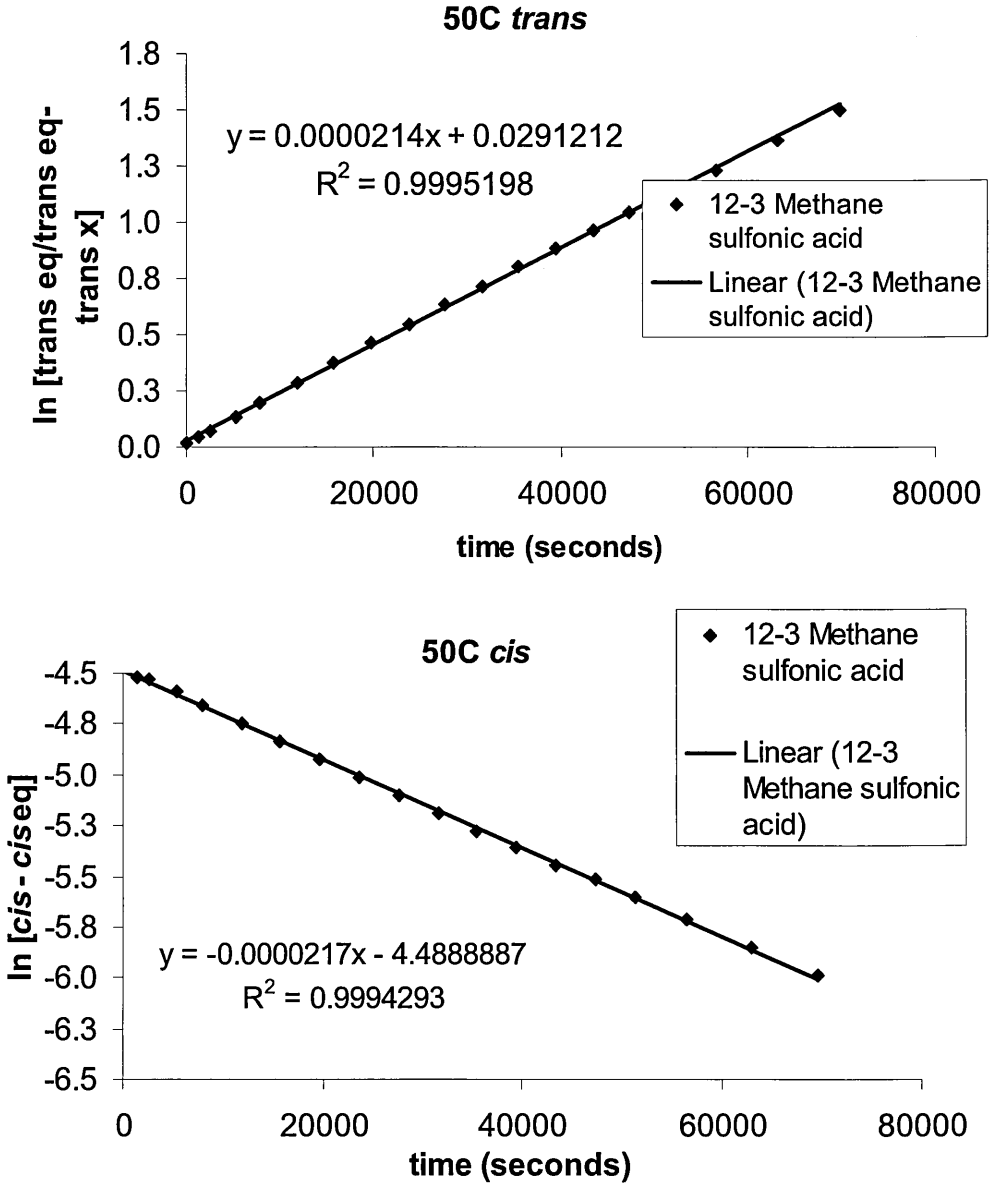


Figure B.11 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 16 mM methanesulphonic acid in nitromethane at 50°C

8-1 Methane sulfonic acid	time (sec)	0	43	2670	5303	7936	10567	13200	15830
	% 2,6-*trans*	0	1.4	8.9	15.2	20.4	24.8	28.5	31.7
area Naphthalene			569.6	571.3	568.3	569.4	570.0	569.9	573.0
area 2,6-*cis*			940.0	877.8	808.1	748.4	702.7	668.3	643.2
area 2,6-*trans*			13.3	85.5	144.8	191.9	232.3	266.8	297.9
Conc. 2,6-*cis*	(mol/L)		0.0224	0.0209	0.0193	0.0178	0.0167	0.0159	0.0152
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0020	0.0035	0.0046	0.0055	0.0064	0.0071
ln [*trans* eq/*trans* eq-*trans* x]			0.0282	0.1946	0.3605	0.5218	0.6830	0.8402	0.9958
ln [*cis-cis* eq]			-4.5016	-4.6605	-4.8321	-5.0086	-5.1765	-5.3334	-5.4880
cis + *trans*	(mol/L)		0.0227	0.0229	0.0228	0.0224	0.0223	0.0223	0.0223
ln [*cis* + *trans*]			-3.7842	-3.7768	-3.7824	-3.7976	-3.8043	-3.8040	-3.8031

8-1 Methane sulfonic acid	time (sec)	18460	21091	23722	26353	28982	34244	39505	47418
	% 2,6-*trans*	34.3	36.6	38.5	40.1	41.5	43.7	45.4	47.0
area Naphthalene		571.8	571.6	574.9	575.9	579.0	577.5	574.8	575.0
area 2,6-*cis*		612.8	592.7	573.7	558.3	550.1	524.3	507.5	485.5
area 2,6-*trans*		320.4	341.8	359.2	374.0	390.6	406.7	422.0	431.4
Conc. 2,6-*cis*	(mol/L)	0.0146	0.0141	0.0136	0.0132	0.0129	0.0123	0.0120	0.0115
Conc. 2,6-*trans*	(mol/L)	0.0076	0.0081	0.0085	0.0088	0.0092	0.0096	0.0100	0.0102
ln [*trans* eq/*trans* eq-*trans* x]		1.1518	1.3042	1.4567	1.6050	1.7553	2.0418	2.3476	2.7686
ln [*cis-cis* eq]		-5.6504	-5.8010	-5.9610	-6.1117	-6.2583	-6.5526	-6.8553	-7.2903
cis + *trans*	(mol/L)	0.0222	0.0222	0.0220	0.0220	0.0221	0.0219	0.0220	0.0217
ln [*cis* + *trans*]		-3.8094	-3.8077	-3.8151	-3.8175	-3.8139	-3.8217	-3.8186	-3.8326

Table B.12 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 60°C

8-2 Methane sulfonic acid	time (sec)	0	1356	3987	6619	9252	11883	14515	17145	19775	22406
	% 2,6-*trans*	0	3.3	7.6	11.5	15.0	18.1	20.9	23.4	25.7	27.9
area Naphthalene			567.0	569.0	567.5	561.7	566.5	565.2	569.3	568.1	567.2
area 2,6-*cis*			926.2	874.6	832.9	796.9	765.2	740.8	713.9	694.4	674.2
area 2,6-*trans*			31.3	72.4	108.3	140.3	168.9	196.1	218.2	240.8	260.4
Conc. 2,6-*cis*	(mol/L)		0.0222	0.0209	0.0199	0.0193	0.0183	0.0178	0.0170	0.0166	0.0161
Conc. 2,6-*trans*	(mol/L)		0.0007	0.0017	0.0026	0.0034	0.0040	0.0047	0.0052	0.0058	0.0062
ln [*trans* eq/*trans* eq-*trans* x]			0.0673	0.1652	0.2603	0.3541	0.4466	0.5395	0.6280	0.7193	0.8097
ln [*cis-cis* eq]			-4.5318	-4.6442	-4.7428	-4.8306	-4.9349	-5.0225	-5.1233	-5.2093	-5.2987
cis + *trans*	(mol/L)		0.0229	0.0226	0.0225	0.0227	0.0224	0.0225	0.0222	0.0224	0.0224
ln [*cis* + *trans*]			-3.7753	-3.7898	-3.7933	-3.7873	-3.7991	-3.7938	-3.8062	-3.8008	-3.7998

8-2 Methane sulfonic acid	time (sec)	25037	27668	30298	32928	35558	38191	43457	46097	51376
	% 2,6-*trans*	29.7	31.4	33.0	34.4	35.6	36.8	38.9	39.8	41.3
area Naphthalene		570.5	566.8	572.1	570.8	568.1	564.5	569.0	569.7	570.5
area 2,6-*cis*		653.5	637.0	627.8	612.1	597.2	581.4	565.0	555.9	541.3
area 2,6-*trans*		276.1	292.1	309.2	320.5	330.7	339.1	360.0	367.7	381.3
Conc. 2,6-*cis*	(mol/L)	0.0156	0.0153	0.0149	0.0146	0.0143	0.0140	0.0135	0.0133	0.0129
Conc. 2,6-*trans*	(mol/L)	0.0066	0.0070	0.0073	0.0076	0.0079	0.0082	0.0086	0.0088	0.0091
ln [*trans* eq/*trans* eq-*trans* x]		0.8956	0.9842	1.0710	1.1539	1.2377	1.3237	1.4929	1.5753	1.7332
ln [*cis-cis* eq]		-5.3958	-5.4784	-5.5661	-5.6513	-5.7355	-5.8231	-5.9954	-6.0805	-6.2409
cis + *trans*	(mol/L)	0.0221	0.0223	0.0222	0.0222	0.0222	0.0221	0.0221	0.0220	0.0220
ln [*cis* + *trans*]		-3.8110	-3.8050	-3.8059	-3.8083	-3.8086	-3.8103	-3.8133	-3.8161	-3.8186

Table B.13 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 60°C

8-3 Methane sulfonic acid	time (sec)	0	47	1361	2677	3994	5309	6626	7944
	% 2,6-*trans*	0	1.8	7.3	12.4	17.0	20.9	24.2	27.2
area Naphthalene			562.6	569.5	570.0	564.7	565.3	563.8	576.4
area 2,6-*cis*			929.5	879.1	829.7	776.1	739.0	702.9	689.2
area 2,6-*trans*			16.7	69.2	117.8	158.5	194.8	224.9	257.8
Conc. 2,6-*cis*	(mol/L)		0.0224	0.0210	0.0198	0.0187	0.0178	0.0169	0.0162
Conc. 2,6-*trans*	(mol/L)		0.0004	0.0016	0.0028	0.0038	0.0047	0.0054	0.0061
ln [*trans* eq/*trans* eq-*trans* x]			0.0358	0.1571	0.2846	0.4122	0.5371	0.6595	0.7815
ln [*cis-cis* eq]			-4.5043	-4.6356	-4.7648	-4.8968	-5.0236	-5.1497	-5.2734
cis + *trans*	(mol/L)		0.0228	0.0226	0.0226	0.0225	0.0224	0.0223	0.0223
ln [*cis* + *trans*]			-3.7793	-3.7893	-3.7910	-3.7954	-3.7973	-3.8011	-3.8027

8-3 Methane sulfonic acid	time (sec)	9262	10580	11896	13212	14527	33078	38338
	% 2,6-*trans*	29.8	32.2	34.1	35.9	37.5	47.7	48.6
area Naphthalene		563.4	567.0	564.6	568.7	571.7	554.6	560.7
area 2,6-*cis*		648.0	628.1	608.9	592.9	580.8	464.1	451.5
area 2,6-*trans*		274.9	298.0	315.7	332.6	348.7	422.8	427.2
Conc. 2,6-*cis*	(mol/L)	0.0156	0.0150	0.0146	0.0142	0.0138	0.0114	0.0109
Conc. 2,6-*trans*	(mol/L)	0.0066	0.0071	0.0076	0.0079	0.0083	0.0104	0.0103
ln [*trans* eq/*trans* eq-*trans* x]		0.8998	1.0244	1.1400	1.2584	1.3756	2.9885	3.4569
ln [*cis-cis* eq]		-5.3947	-5.5222	-5.6351	-5.7598	-5.8779	-7.5074	-7.9960
cis + *trans*	(mol/L)	0.0222	0.0222	0.0222	0.0221	0.0221	0.0217	0.0213
ln [*cis* + *trans*]		-3.8057	-3.8086	-3.8060	-3.8123	-3.8132	-3.8297	-3.8500

Table B.14 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 29 mM methanesulphonic acid in nitromethane at 60°C

9-1 Methane sulfonic acid	time (sec)	0	286	2913	5544	8175	10807	13436	16066	18694	21323
	% 2,6-*trans*	0	1.4	7.6	12.7	17.2	21.0	24.4	27.3	29.8	32.1
area Naphthalene			560.4	564.9	563.4	562.1	560.9	562.7	563.1	561.5	567.7
area 2,6-*cis*			909.5	857.4	809.9	765.5	725.5	697.6	669.3	643.7	627.2
area 2,6-*trans*			12.7	70.1	118.1	158.8	192.8	225.1	251.1	273.9	296.6
Conc. 2,6-*cis*	(mol/L)		0.0220	0.0206	0.0195	0.0185	0.0176	0.0168	0.0161	0.0156	0.0150
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0017	0.0028	0.0038	0.0047	0.0054	0.0061	0.0066	0.0071
ln [*trans* eq/*trans* eq-*trans* x]			0.0278	0.1632	0.2924	0.4189	0.5417	0.6655	0.7841	0.9029	1.0205
ln [*cis*-*cis* eq]			-4.5181	-4.6557	-4.7817	-4.9100	-5.0371	-5.1593	-5.2811	-5.4002	-5.5220
cis + *trans*	(mol/L)		0.0223	0.0223	0.0224	0.0223	0.0222	0.0223	0.0222	0.0222	0.0221
ln [*cis* + *trans*]			-3.8011	-3.8034	-3.8002	-3.8019	-3.8063	-3.8047	-3.8079	-3.8081	-3.8123

9-1 Methane sulfonic acid	time (sec)	23952	26582	29212	31843	34474	37106	55519	87077	100211
	% 2,6-*trans*	34.1	35.8	37.4	38.8	40.0	41.1	45.9	49.0	49.5
area Naphthalene		565.2	568.5	567.5	564.1	561.4	558.1	549.1	558.8	562.9
area 2,6-*cis*		602.5	589.4	571.7	556.4	540.9	527.3	466.8	440.5	434.4
area 2,6-*trans*		312.4	329.3	342.1	352.1	360.6	367.5	395.7	422.8	425.4
Conc. 2,6-*cis*	(mol/L)	0.0145	0.0141	0.0137	0.0134	0.0131	0.0128	0.0115	0.0107	0.0105
Conc. 2,6-*trans*	(mol/L)	0.0075	0.0079	0.0082	0.0085	0.0087	0.0089	0.0098	0.0103	0.0103
ln [*trans* eq/*trans* eq-*trans* x]		1.1400	1.2519	1.3695	1.4786	1.5936	1.7045	2.4524	3.7130	4.2398
ln [*cis*-*cis* eq]		-5.6468	-5.7603	-5.8815	-5.9904	-6.1084	-6.2208	-6.9892	-8.2664	-8.8046
cis + *trans*	(mol/L)	0.0220	0.0219	0.0219	0.0219	0.0218	0.0218	0.0213	0.0210	0.0207
ln [*cis* + *trans*]		-3.8176	-3.8193	-3.8229	-3.8227	-3.8256	-3.8272	-3.8477	-3.8643	-3.8756

Table B.15 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 22 mM methanesulphonic acid in nitromethane at 60°C

9-2 Methane sulfonic acid	time (sec)	0	1599	4228	6859	9492	12122	14751	17381	20009	22638	25266
	% 2,6-*trans*	0	0.6	6.1	9.1	11.8	14.4	16.7	18.8	20.8	22.6	24.3
area Naphthalene			551.4	560.6	551.9	554.3	551.2	556.5	555.2	558.9	561.2	562.9
area 2,6-*cis*			903.1	867.5	830.5	806.4	780.1	764.5	738.5	727.0	713.1	696.6
area 2,6-*trans*			5.1	56.1	82.9	108.2	130.8	153.1	171.3	191.4	208.7	224.0
Conc. 2,6-*cis*	(mol/L)		0.0222	0.0210	0.0204	0.0198	0.0192	0.0187	0.0181	0.0177	0.0173	0.0168
Conc. 2,6-*trans*	(mol/L)		0.0001	0.0014	0.0020	0.0027	0.0032	0.0037	0.0042	0.0047	0.0050	0.0054
ln [*trans* eq/*trans* eq-*trans* x]			0.0112	0.1290	0.1994	0.2687	0.3369	0.4040	0.4701	0.5364	0.5997	0.6630
ln [*cis-cis* eq]			-4.5006	-4.6181	-4.6840	-4.7564	-4.8230	-4.8923	-4.9646	-5.0281	-5.0918	-5.1595
cis + *trans*	(mol/L)		0.0224	0.0224	0.0225	0.0224	0.0224	0.0224	0.0223	0.0223	0.0223	0.0222
ln [*cis* + *trans*]			-3.8002	-3.8000	-3.7954	-3.7985	-3.7969	-3.7991	-3.8053	-3.8026	-3.8030	-3.8073

9-2 Methane sulfonic acid	time (sec)	30528	33159	35790	38421	43682	48944	56834	64717	75245	88391	98897
	% 2,6-*trans*	27.4	28.8	30.1	31.2	33.4	35.2	37.7	39.7	41.8	43.8	45.1
area Naphthalene		558.6	557.3	557.1	559.1	552.9	558.8	548.6	554.6	551.7	547.3	544.0
area 2,6-*cis*		661.3	647.5	622.0	618.6	590.5	579.9	544.7	535.3	513.1	487.8	472.2
area 2,6-*trans*		250.0	261.9	267.3	280.8	295.5	315.5	329.3	351.8	368.4	380.9	387.6
Conc. 2,6-*cis*	(mol/L)	0.0161	0.0158	0.0152	0.0150	0.0145	0.0141	0.0135	0.0131	0.0126	0.0121	0.0118
Conc. 2,6-*trans*	(mol/L)	0.0061	0.0064	0.0065	0.0068	0.0073	0.0077	0.0082	0.0086	0.0091	0.0095	0.0097
ln [*trans* eq/*trans* eq-*trans* x]		0.7907	0.8526	0.9132	0.9727	1.0918	1.2103	1.3885	1.5606	1.7869	2.0671	2.2829
ln [*cis-cis* eq]		-5.2897	-5.3513	-5.4339	-5.4857	-5.6086	-5.7273	-5.9112	-6.0793	-6.3066	-6.5935	-6.8135
cis + *trans*	(mol/L)	0.0222	0.0222	0.0217	0.0218	0.0218	0.0218	0.0216	0.0217	0.0217	0.0216	0.0215
ln [*cis* + *trans*]		-3.8098	-3.8096	-3.8315	-3.8238	-3.8277	-3.8278	-3.8335	-3.8295	-3.8306	-3.8372	-3.8415

Table B.16 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 17 mM methanesulphonic acid in nitromethane at 60°C

9-3 Methane sulfonic acid	time (sec)	0	203	2832	5460	8089	10718	13350	18612	23877	29142	34404
	% 2,6-*trans*	0	0.9	3.1	5.2	7.2	9.1	10.9	14.2	17.1	19.8	22.2
area Naphthalene			566.1	564.7	562.2	563.5	564.7	567.7	565.0	560.6	560.3	563.9
area 2,6-*cis*			940.4	916.7	895.3	877.0	858.0	844.0	810.8	778.2	751.0	729.5
area 2,6-*trans*			8.8	29.1	49.1	68.2	85.9	102.9	134.0	160.7	184.9	207.8
Conc. 2,6-*cis*	(mol/L)		0.0226	0.0220	0.0216	0.0211	0.0206	0.0202	0.0195	0.0188	0.0182	0.0176
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0007	0.0012	0.0016	0.0021	0.0025	0.0032	0.0039	0.0045	0.0050
ln [*trans* eq/*trans* eq-*trans* x]			0.0186	0.0632	0.1093	0.1552	0.2000	0.2440	0.3320	0.4170	0.5001	0.5827
ln [*cis*-*cis* eq]			-4.4902	-4.5359	-4.5790	-4.6263	-4.6747	-4.7207	-4.8063	-4.8896	-4.9755	-5.0630
cis + *trans*	(mol/L)		0.0228	0.0227	0.0228	0.0228	0.0227	0.0226	0.0227	0.0227	0.0227	0.0226
ln [*cis* + *trans*]			-3.7824	-3.7835	-3.7805	-3.7820	-3.7855	-3.7876	-3.7851	-3.7835	-3.7862	-3.7911

9-3 Methane sulfonic acid	time (sec)	39667	44930	50195	55468	60736	66006	71278	76547	81829	87094
	% 2,6-*trans*	24.3	26.3	28.1	29.6	31.2	32.5	33.8	34.9	36.0	36.9
area Naphthalene		560.9	558.7	558.0	556.8	558.2	563.3	557.0	560.8	558.3	558.2
area 2,6-*cis*		706.3	684.5	664.7	648.4	635.6	625.8	606.8	602.1	587.7	576.6
area 2,6-*trans*		226.8	244.2	259.5	273.1	288.0	301.7	309.5	323.0	330.0	337.4
Conc. 2,6-*cis*	(mol/L)	0.0171	0.0166	0.0162	0.0158	0.0155	0.0151	0.0148	0.0146	0.0143	0.0140
Conc. 2,6-*trans*	(mol/L)	0.0055	0.0059	0.0063	0.0067	0.0070	0.0073	0.0075	0.0078	0.0080	0.0082
ln [*trans* eq/*trans* eq-*trans* x]		0.6620	0.7419	0.8195	0.8925	0.9706	1.0441	1.1173	1.1892	1.2599	1.3294
ln [*cis*-*cis* eq]		-5.1414	-5.2221	-5.3033	-5.3771	-5.4555	-5.5338	-5.6080	-5.6770	-5.7513	-5.8246
cis + *trans*	(mol/L)	0.0226	0.0226	0.0225	0.0225	0.0225	0.0224	0.0223	0.0224	0.0223	0.0222
ln [*cis* + *trans*]		-3.7903	-3.7911	-3.7947	-3.7954	-3.7957	-3.8006	-3.8015	-3.7987	-3.8023	-3.8061

Table B.17 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 14 mM methanesulphonic acid in nitromethane at 60°C

9-4 Methane sulfonic acid	time (sec)	0	1517	4146	6775	9404	12034	14666	19929	25194	30457	35720
	% 2,6-trans	0	1.4	2.8	4.1	5.4	6.7	7.8	10.1	12.2	14.2	16.0
area Naphthalene			564.0	559.0	559.6	559.4	560.1	557.1	557.4	559.5	560.8	558.8
area 2,6-*cis*			936.4	913.2	901.8	888.9	876.4	864.1	840.7	824.7	804.1	785.7
area 2,6-*trans*			13.3	26.0	38.8	50.9	62.5	73.5	94.3	114.4	132.6	149.6
Conc. 2,6-*cis*	(mol/L)		0.0231	0.0227	0.0224	0.0221	0.0218	0.0216	0.0210	0.0205	0.0199	0.0195
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0006	0.0010	0.0013	0.0016	0.0018	0.0024	0.0028	0.0033	0.0037
ln [*trans* eq/*trans* eq-*trans* x]			0.0283	0.0567	0.0857	0.1142	0.1423	0.1698	0.2243	0.2780	0.3313	0.3836
ln [*cis-cis* eq]			-4.4720	-4.5026	-4.5312	-4.5601	-4.5904	-4.6140	-4.6718	-4.7248	-4.7830	-4.8333
cis + *trans*	(mol/L)		0.0234	0.0234	0.0234	0.0234	0.0233	0.0234	0.0233	0.0233	0.0232	0.0233
ln [*cis* + *trans*]			-3.7545	-3.7567	-3.7563	-3.7568	-3.7590	-3.7550	-3.7583	-3.7577	-3.7626	-3.7605

9-4 Methane sulfonic acid	time (sec)	40983	46246	51512	56785	62055	67325	72596	77864	83128	88396
	% 2,6-*trans*	17.7	19.3	20.8	22.2	23.6	24.8	26.0	27.2	28.3	29.3
area Naphthalene		562.8	564.4	563.2	561.1	565.7	569.5	572.4	580.5	584.6	592.1
area 2,6-*cis*		773.9	760.5	745.8	726.9	720.2	713.5	703.9	702.3	695.4	693.6
area 2,6-*trans*		166.4	181.8	195.6	207.7	222.1	235.9	247.9	262.0	274.0	287.7
Conc. 2,6-*cis*	(mol/L)	0.0191	0.0187	0.0184	0.0180	0.0177	0.0174	0.0171	0.0168	0.0165	0.0163
Conc. 2,6-*trans*	(mol/L)	0.0041	0.0045	0.0048	0.0051	0.0055	0.0058	0.0060	0.0063	0.0065	0.0068
ln [*trans* eq/*trans* eq-*trans* x]		0.4347	0.4850	0.5343	0.5846	0.6340	0.6831	0.7315	0.7792	0.8279	0.8771
ln [*cis-cis* eq]		-4.8861	-4.9372	-4.9853	-5.0392	-5.0885	-5.1368	-5.1878	-5.2365	-5.2869	-5.3367
cis + *trans*	(mol/L)	0.0232	0.0232	0.0232	0.0232	0.0232	0.0232	0.0231	0.0231	0.0231	0.0230
ln [*cis* + *trans*]		-3.7623	-3.7630	-3.7619	-3.7654	-3.7653	-3.7645	-3.7671	-3.7681	-3.7698	-3.7704

Table B.18 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 12 mM methanesulphonic acid in nitromethane at 60°C

10-1 Methane sulfonic acid	time (sec)	0	98	1414	2730	4045	5361	6677	7994	9310	10627	11945
	% 2,6-*trans*	0	1.5	5.7	9.7	13.3	16.5	19.4	22.1	24.5	26.7	28.7
area Naphthalene			554.8	555.5	558.4	551.1	548.9	550.4	549.7	550.8	548.6	551.4
area 2,6-*cis*			921.9	881.2	847.2	797.8	765.5	739.3	712.3	688.9	669.2	651.9
area 2,6-*trans*			14.2	53.2	90.6	121.9	151.2	178.3	202.3	224.1	244.0	262.8
Conc. 2,6-*cis*	(mol/L)		0.0226	0.0215	0.0206	0.0197	0.0189	0.0182	0.0176	0.0170	0.0166	0.0161
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0013	0.0022	0.0030	0.0037	0.0044	0.0050	0.0055	0.0060	0.0065
ln [*trans* eq/*trans* eq-*trans* x]			0.0307	0.1204	0.2137	0.3066	0.3983	0.4895	0.5809	0.6713	0.7598	0.8494
ln [*cis*-*cis* eq]			-4.4960	-4.5887	-4.6837	-4.7828	-4.8739	-4.9668	-5.0602	-5.1543	-5.2386	-5.3316
cis + *trans*	(mol/L)		0.0229	0.0228	0.0228	0.0227	0.0227	0.0226	0.0226	0.0225	0.0226	0.0225
ln [*cis* + *trans*]			-3.7761	-3.7792	-3.7808	-3.7871	-3.7864	-3.7881	-3.7901	-3.7939	-3.7896	-3.7931

10-1 Methane sulfonic acid	time (sec)	17210	18526	19843	21159	22476	23792	29057	34318	40894	46152	51432
	% 2,6-*trans*	35.0	36.3	37.4	38.4	39.4	40.3	43.0	45.0	46.7	47.7	48.3
area Naphthalene		549.2	550.2	549.1	547.2	548.5	550.1	549.0	545.3	553.5	557.3	557.9
area 2,6-*cis*		586.2	576.1	563.7	554.9	544.2	535.1	507.8	486.7	473.9	465.0	456.0
area 2,6-*trans*		316.2	328.0	337.1	346.6	353.7	360.8	383.6	398.7	415.6	423.6	426.3
Conc. 2,6-*cis*	(mol/L)	0.0145	0.0142	0.0139	0.0138	0.0135	0.0132	0.0126	0.0121	0.0116	0.0113	0.0111
Conc. 2,6-*trans*	(mol/L)	0.0078	0.0081	0.0083	0.0086	0.0088	0.0089	0.0095	0.0099	0.0102	0.0103	0.0104
ln [*trans* eq/*trans* eq-*trans* x]		1.1973	1.2826	1.3683	1.4519	1.5357	1.6207	1.9466	2.2732	2.6698	2.9880	3.2831
ln [*cis*-*cis* eq]		-5.6891	-5.7744	-5.8617	-5.9411	-6.0312	-6.1214	-6.4503	-6.7769	-7.1838	-7.5098	-7.8131
cis + *trans*	(mol/L)	0.0223	0.0223	0.0223	0.0224	0.0222	0.0221	0.0220	0.0220	0.0218	0.0217	0.0215
ln [*cis* + *trans*]		-3.8026	-3.8026	-3.8042	-3.8000	-3.8064	-3.8115	-3.8145	-3.8145	-3.8248	-3.8327	-3.8409

Table B.19 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 26 mM methanesulphonic acid in nitromethane at 60°C

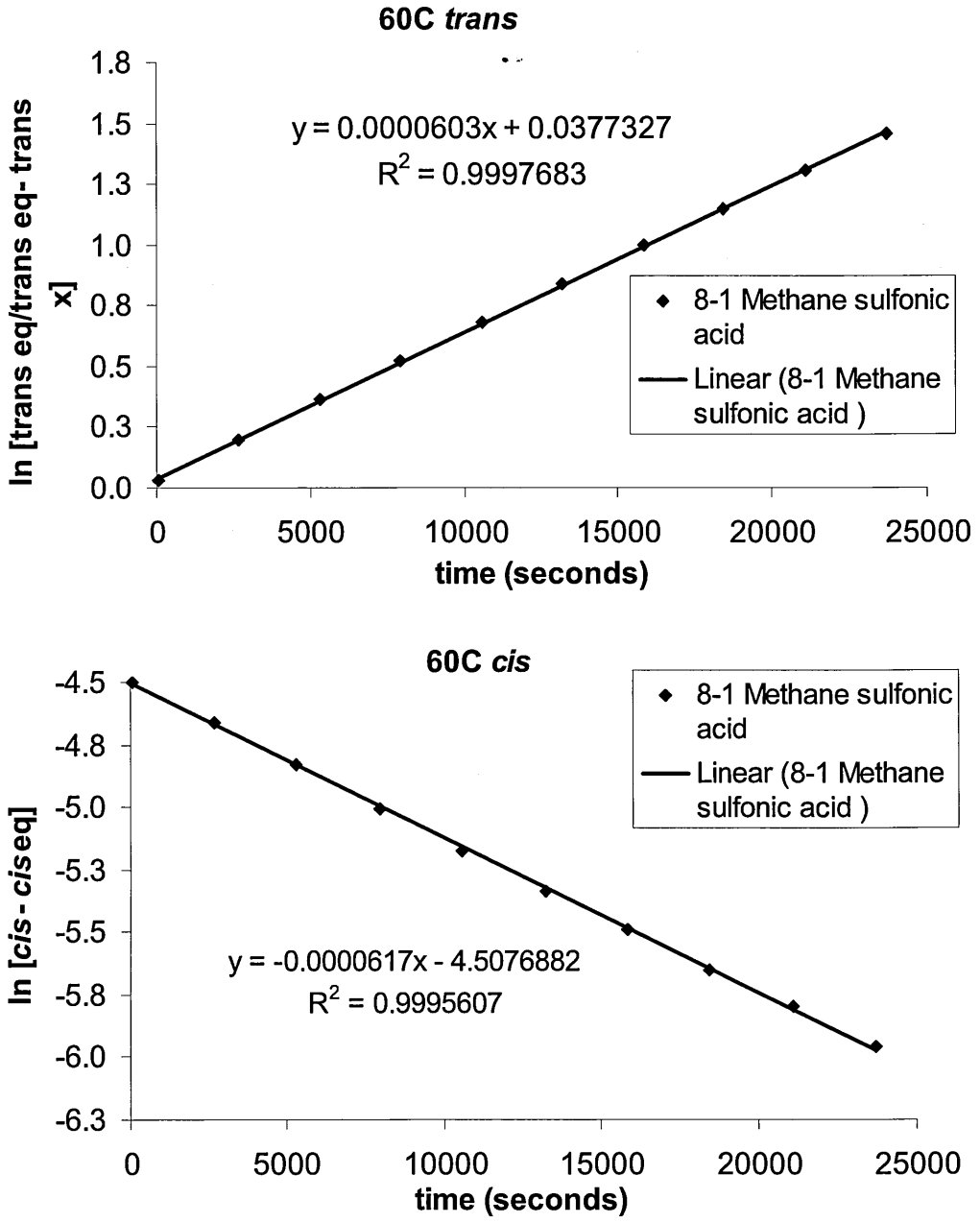


Figure B.12 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 60°C

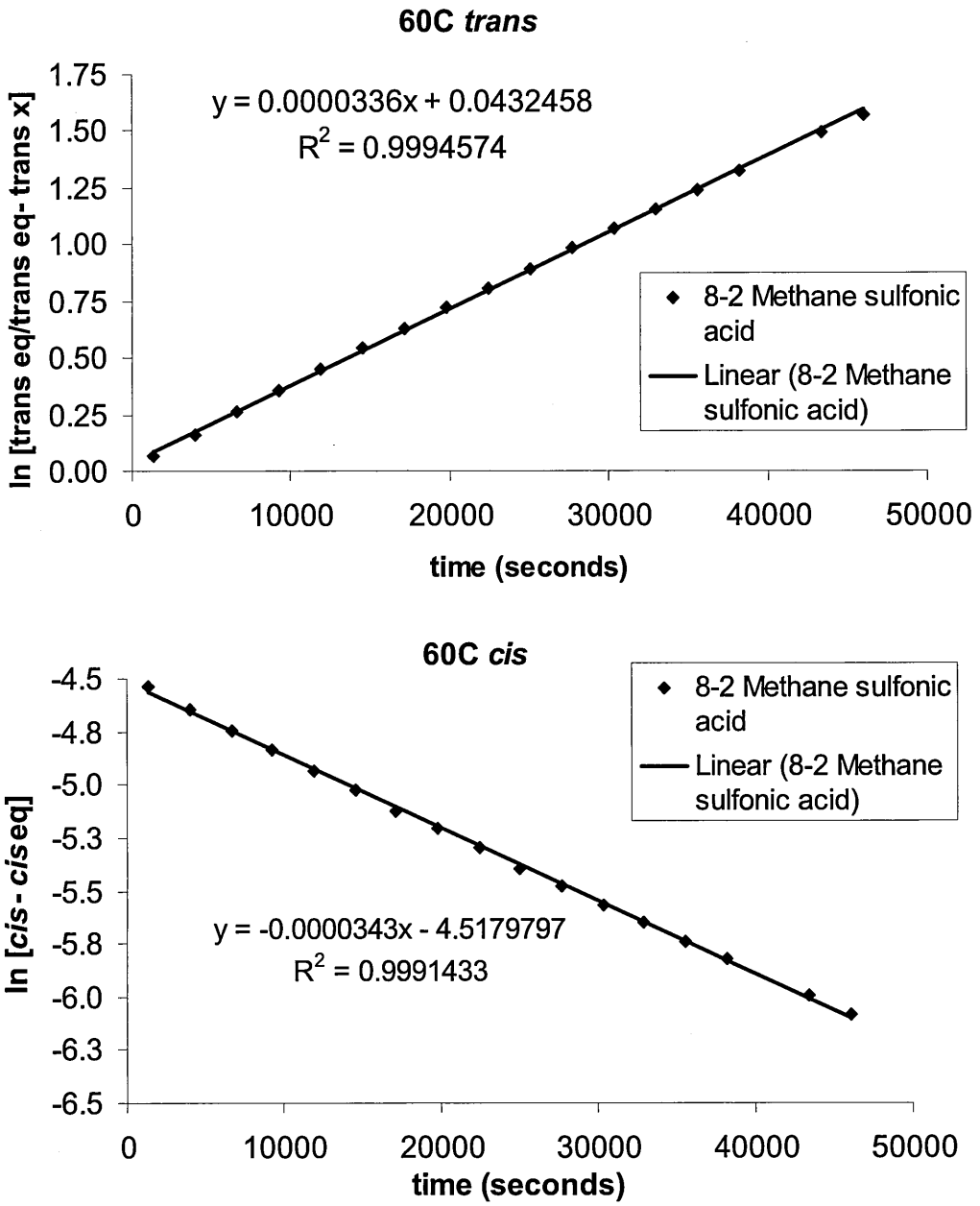


Figure B.13 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 60°C

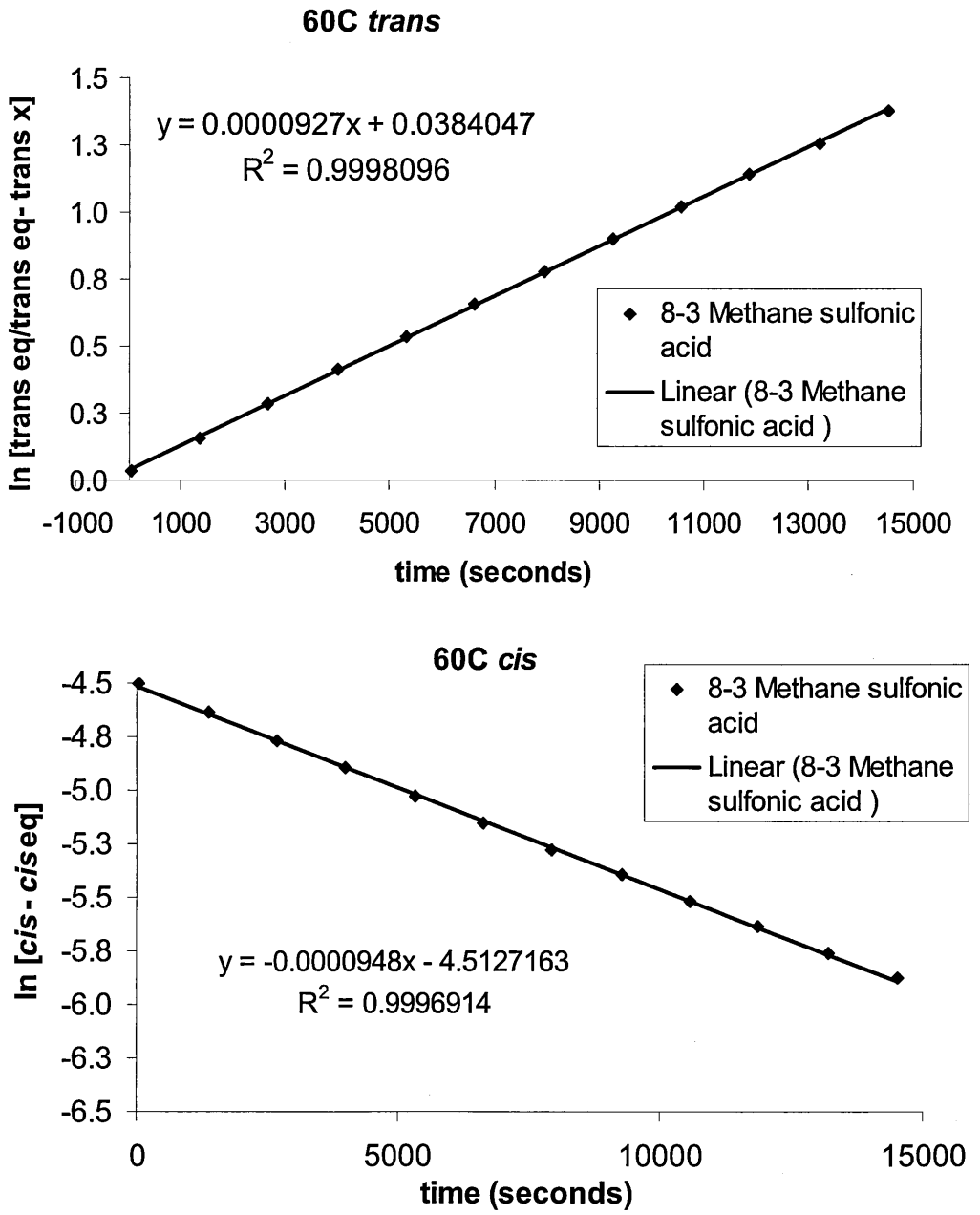


Figure B.14 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 29 mM methanesulphonic acid in nitromethane at 60°C

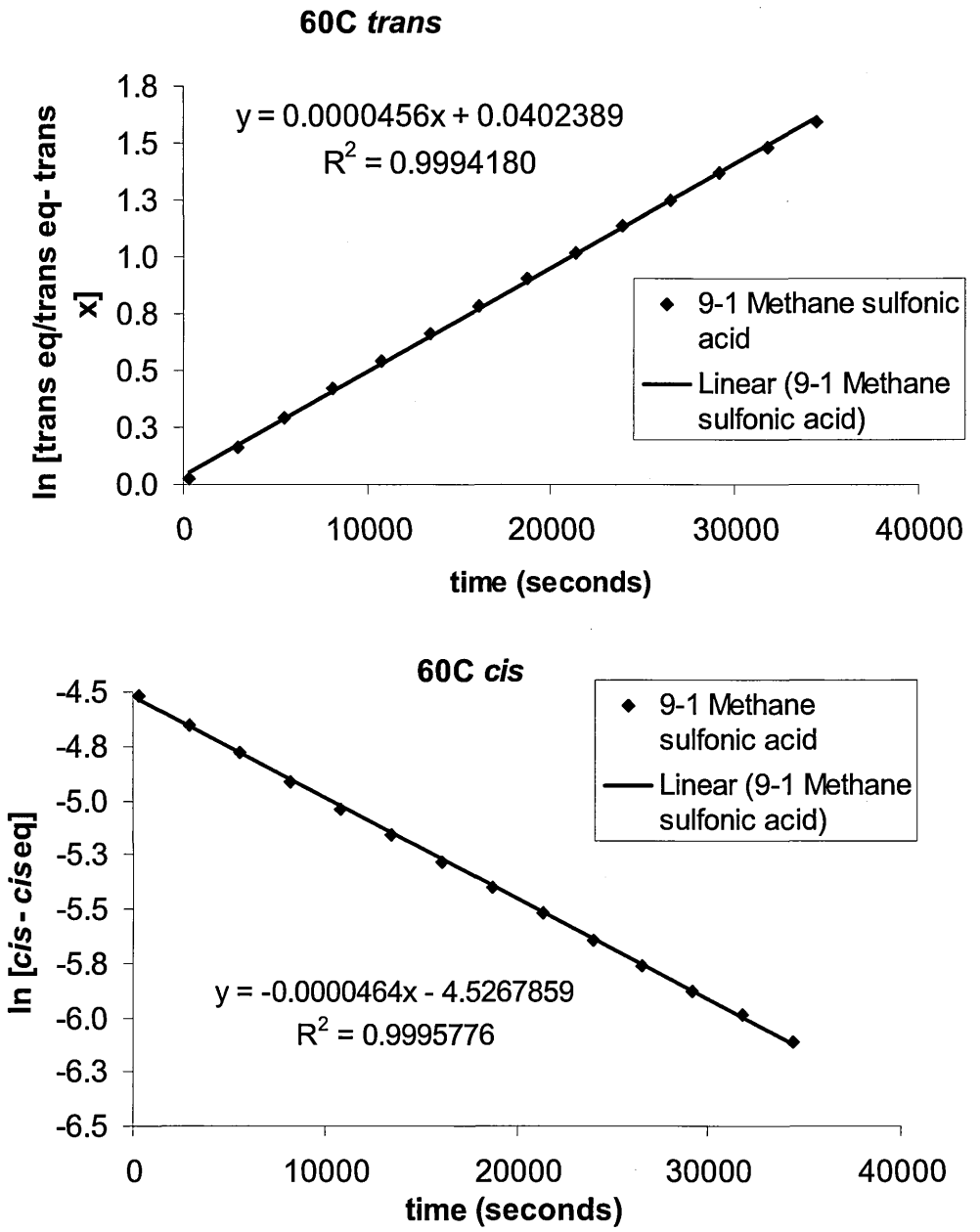


Figure B.15 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 22 mM methanesulphonic acid in nitromethane at 60°C

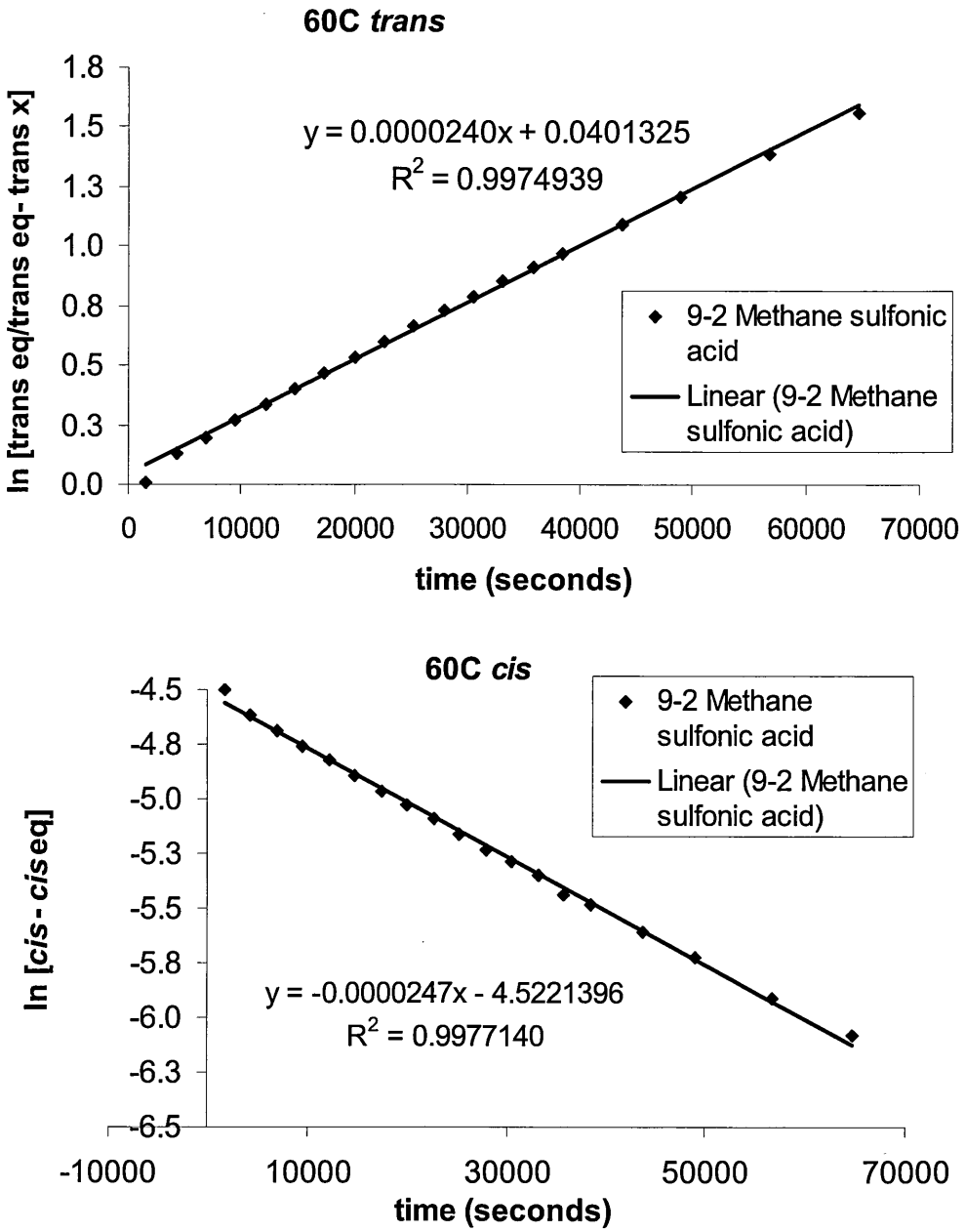


Figure B.16 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 17 mM methanesulphonic acid in nitromethane at 60°C

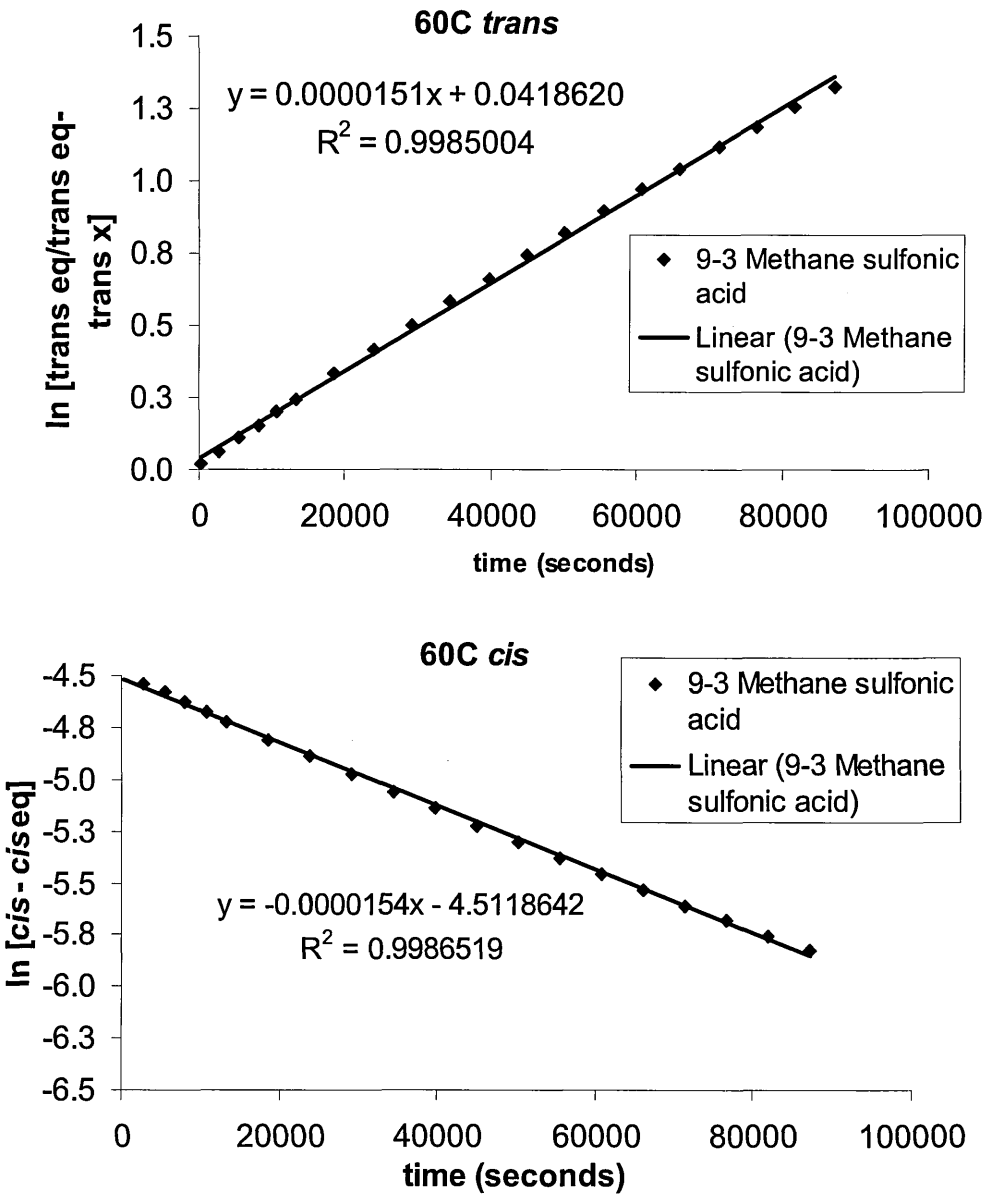


Figure B.17 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 14 mM methanesulphonic acid in nitromethane at 60°C

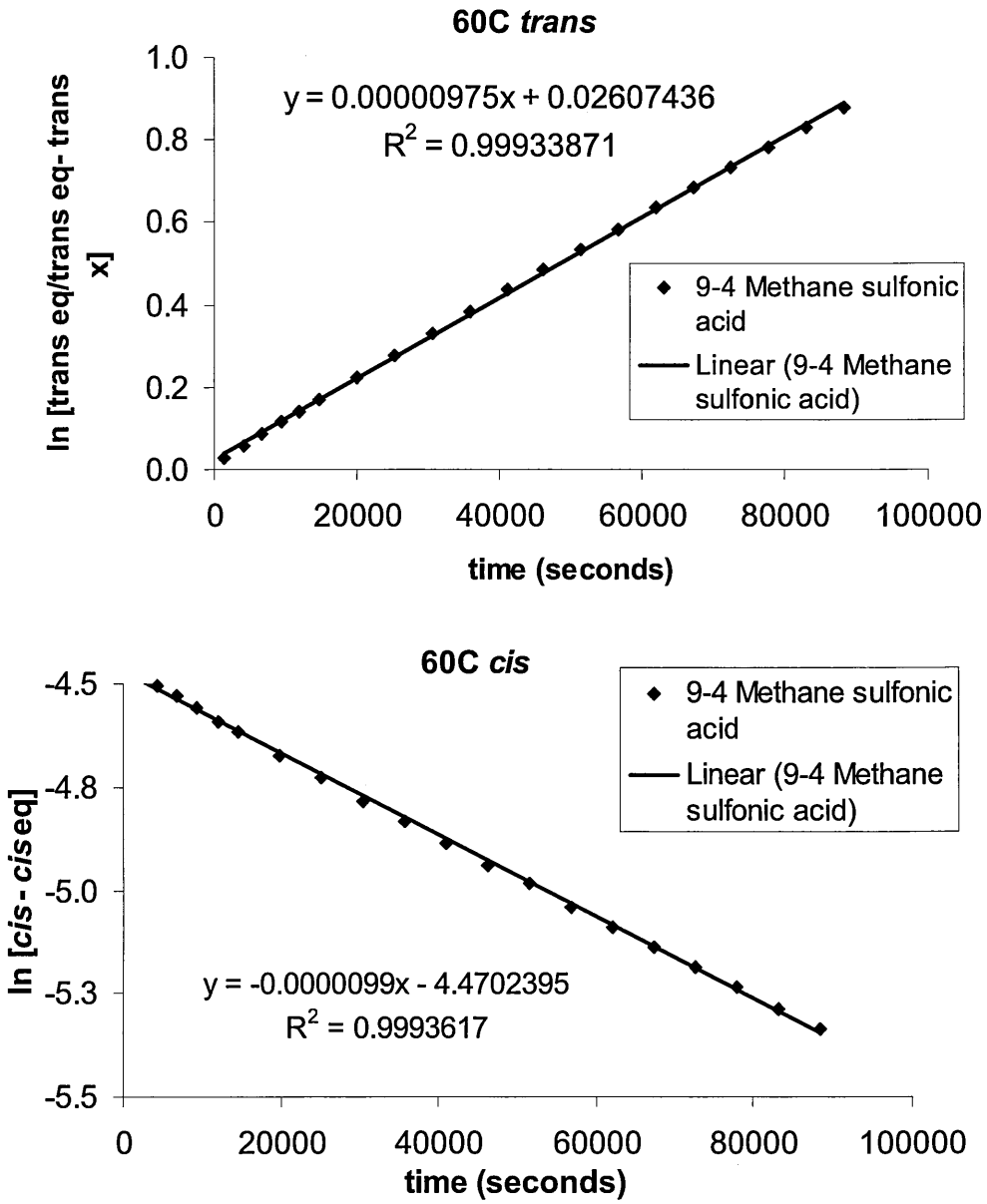


Figure B.18 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 12 mM methanesulphonic acid in nitromethane at 60°C

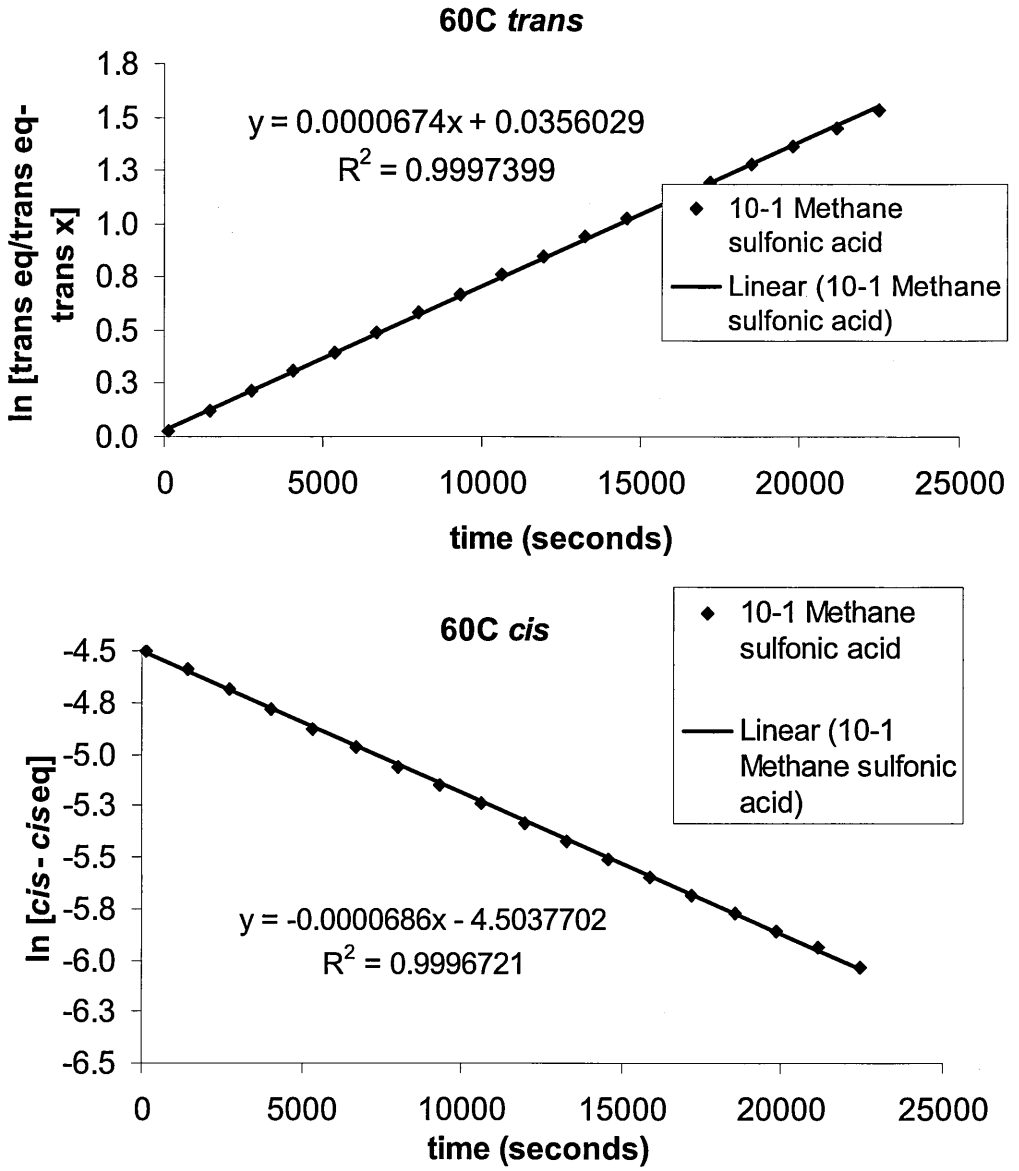


Figure B.19 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 26 mM methanesulphonic acid in nitromethane at 60°C

5-1 Methane sulfonic acid	time (sec)	0	91	4032	7979	11924	15873
0.035M cat.	% 2,6-*trans*	0	3.5	29.1	40.3	45.4	47.7
area Naphthalene			549.9	544.1	543.3	543.7	544.7
area 2,6-*cis*			879.5	639.2	530.8	474.2	448.5
area 2,6-*trans*			31.6	261.9	358.6	394.0	409.8
Conc. 2,6-*cis*	(mol/L)		0.0217	0.0160	0.0133	0.0118	0.0112
Conc. 2,6-*trans*	(mol/L)		0.0008	0.0065	0.0090	0.0098	0.0102
ln [*trans* eq/*trans* eq-*trans* x]			0.0716	0.8651	1.6254	2.3435	3.0181
ln [*cis*-*cis* eq]			-4.5551	-5.3490	-6.1209	-6.8639	-7.5518
cis + *trans*	(mol/L)		0.0225	0.0225	0.0222	0.0217	0.0214
ln [*cis* + *trans*]			-3.7943	-3.7948	-3.8063	-3.8312	-3.8445

5-1 Methane sulfonic acid	time (sec)	19822	39572	55382	94891	178476
0.035M cat.	% 2,6-*trans*	48.9	50.0	50.1	50.2	50.2
area Naphthalene		544.3	543.6	541.2	553.0	554.1
area 2,6-*cis*		433.1	395.6	375.1	337.8	263.1
area 2,6-*trans*		414.3	396.3	376.8	340.2	265.4
Conc. 2,6-*cis*	(mol/L)	0.0108	0.0099	0.0094	0.0085	0.0066
Conc. 2,6-*trans*	(mol/L)	0.0103	0.0099	0.0095	0.0086	0.0067
ln [*trans* eq/*trans* eq-*trans* x]		3.6465	5.7752	6.3584	7.6879	#NUM!
ln [*cis*-*cis* eq]		-8.1923	-10.3873	-11.0180	-12.4489	#NUM!
cis + *trans*	(mol/L)	0.0211	0.0198	0.0189	0.0170	0.0133
ln [*cis* + *trans*]		-3.8566	-3.9230	-3.9704	-4.0718	-4.3229

Table B.20 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 36 mM methanesulphonic acid in nitromethane at 70°C

5-2 Methane sulfonic acid	time (sec)	0	1403	5347	9294	13241	17188	21137
0.024M cat.	% 2,6-*trans*	0	6.6	18.4	26.7	32.7	37.0	40.2
area Naphthalene			543.9	544.8	545.7	546.4	545.9	549.4
area 2,6-*cis*			858.9	744.1	661.7	605.9	563.0	530.6
area 2,6-*trans*			60.5	168.1	241.4	294.6	331.2	357.0
Conc. 2,6-*cis*	(mol/L)		0.0214	0.0185	0.0165	0.0151	0.0140	0.0131
Conc. 2,6-*trans*	(mol/L)		0.0015	0.0042	0.0060	0.0073	0.0082	0.0088
ln [*trans* eq/*trans* eq-*trans* x]			0.1405	0.4574	0.7603	1.0547	1.3387	1.6155
ln [*cis*-*cis* eq]			-4.6039	-4.9304	-5.2449	-5.5435	-5.8336	-6.1242
cis + *trans*	(mol/L)		0.0230	0.0227	0.0225	0.0224	0.0222	0.0219
ln [*cis* + *trans*]			-3.774	-3.784	-3.795	-3.800	-3.806	-3.820

5-2 Methane sulfonic acid	time (sec)	25088	36939	40889	56699	96206	179792
0.024M cat.	% 2,6-*trans*	42.5	46.8	47.6	49.3	50.2	50.3
area Naphthalene		555.1	571.6	574.8	576.7	586.1	604.9
area 2,6-*cis*		514.7	482.6	474.3	450.7	421.4	374.3
area 2,6-*trans*		380.2	424.2	430.2	437.7	424.6	378.4
Conc. 2,6-*cis*	(mol/L)	0.0126	0.0115	0.0112	0.0106	0.0098	0.0084
Conc. 2,6-*trans*	(mol/L)	0.0093	0.0101	0.0102	0.0103	0.0098	0.0085
ln [*trans* eq/*trans* eq-*trans* x]		1.8729	2.6863	2.9461	3.9868	8.4373	#NUM!
ln [*cis*-*cis* eq]		-6.3837	-7.2132	-7.4811	-8.5431	-13.0587	#NUM!
cis + *trans*	(mol/L)	0.0219	0.0215	0.0214	0.0209	0.0196	0.0169
ln [*cis* + *trans*]		-3.822	-3.838	-3.846	-3.867	-3.932	-4.081

Table B.21 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 70°C

5-3 Methane sulfonic acid	time (sec)	0	2718	6663	10609	18506	22455	26407
0.012M cat.	% 2,6-*trans*	0	3.0	6.1	9.0	14.0	16.1	18.1
area Naphthalene			549.4	540.2	541.8	541.0	543.1	540.4
area 2,6-*cis*			888.3	857.8	828.5	781.5	761.8	737.5
area 2,6-*trans*			27.4	56.2	81.8	127.0	146.3	163.4
Conc. 2,6-*cis*	(mol/L)		0.0220	0.0216	0.0208	0.0196	0.0190	0.0185
Conc. 2,6-*trans*	(mol/L)		0.0007	0.0014	0.0021	0.0032	0.0037	0.0041
ln [*trans* eq/*trans* eq-*trans* x]			0.0615	0.1307	0.1972	0.3264	0.3870	0.4483
ln [*cis*-*cis* eq]			-4.5390	-4.5932	-4.6668	-4.7964	-4.8614	-4.9256
cis + *trans*	(mol/L)		0.0226	0.0230	0.0228	0.0228	0.0227	0.0226
ln [*cis* + *trans*]			-3.7884	-3.7733	-3.7804	-3.7809	-3.7852	-3.7882

5-3 Methane sulfonic acid	time (sec)	38256	50109	58017	61971	77775	93575	181107
0.012M cat.	% 2,6-*trans*	23.2	27.2	29.4	30.5	34.1	37.1	45.5
area Naphthalene		540.1	538.7	546.7	543.6	548.8	567.6	566.4
area 2,6-*cis*		686.9	646.8	631.5	619.4	586.9	577.7	479.7
area 2,6-*trans*		207.7	241.4	263.6	271.6	304.1	340.5	400.6
Conc. 2,6-*cis*	(mol/L)	0.0173	0.0163	0.0157	0.0155	0.0145	0.0138	0.0115
Conc. 2,6-*trans*	(mol/L)	0.0052	0.0061	0.0065	0.0068	0.0075	0.0081	0.0096
ln [*trans* eq/*trans* eq-*trans* x]		0.6208	0.7796	0.8834	0.9345	1.1391	1.3421	2.3700
ln [*cis*-*cis* eq]		-5.1046	-5.2679	-5.3788	-5.4288	-5.6429	-5.8495	-6.9174
cis + *trans*	(mol/L)	0.0225	0.0224	0.0222	0.0223	0.0220	0.0220	0.0211
ln [*cis* + *trans*]		-3.7946	-3.7992	-3.8062	-3.8051	-3.8146	-3.8182	-3.8583

Table B.22 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 12 mM methanesulphonic acid in nitromethane at 70°C

6-1 Methane sulfonic acid	time (sec)	0	39	3987	7939	11887	15835	19786	23734	27678
	% 2,6-*trans*	0	1.7	9.6	16.0	21.3	25.6	29.2	32.2	34.6
area Naphthalene			550.7	544.5	544.8	543.5	545.3	543.8	547.5	547.0
area 2,6-*cis*			913.2	831.7	767.3	713.3	674.2	635.5	609.6	584.7
area 2,6-*trans*			16.2	88.2	146.5	192.6	231.4	261.5	289.0	309.8
Conc. 2,6-*cis*	(mol/L)		0.0225	0.0207	0.0191	0.0178	0.0168	0.0159	0.0151	0.0145
Conc. 2,6-*trans*	(mol/L)		0.0004	0.0022	0.0037	0.0048	0.0058	0.0065	0.0072	0.0077
ln [*trans* eq/*trans* eq-*trans* x]			0.0353	0.2120	0.3847	0.5508	0.7113	0.8692	1.0235	1.1709
ln [*cis*-*cis* eq]			-4.5004	-4.6759	-4.8559	-5.0283	-5.1925	-5.3572	-5.5164	-5.6675
cis + *trans*	(mol/L)		0.0229	0.0229	0.0228	0.0226	0.0226	0.0224	0.0223	0.0222
ln [*cis* + *trans*]			-3.7759	-3.7748	-3.7820	-3.7883	-3.7920	-3.7988	-3.8038	-3.8074

6-1 Methane sulfonic acid	time (sec)	31623	35567	39527	43485	51394	63237	75077	84022	174736
	% 2,6-*trans*	36.8	38.6	40.1	41.4	43.5	45.7	47.2	47.9	50.1
area Naphthalene		550.1	544.6	546.2	545.0	545.5	547.2	544.8	545.2	546.5
area 2,6-*cis*		565.8	543.0	529.1	514.1	491.1	467.7	449.4	438.3	386.2
area 2,6-*trans*		328.8	340.7	353.6	362.7	378.1	393.8	401.1	403.4	388.0
Conc. 2,6-*cis*	(mol/L)	0.0140	0.0135	0.0132	0.0128	0.0122	0.0116	0.0112	0.0109	0.0096
Conc. 2,6-*trans*	(mol/L)	0.0081	0.0085	0.0088	0.0090	0.0094	0.0098	0.0100	0.0100	0.0096
ln [*trans* eq/*trans* eq-*trans* x]		1.3173	1.4610	1.5994	1.7374	2.0139	2.4144	2.8043	3.0948	6.3959
ln [*cis*-*cis* eq]		-5.8194	-5.9654	-6.1078	-6.2503	-6.5364	-6.9489	-7.3473	-7.6490	-11.0360
cis + *trans*	(mol/L)	0.0221	0.0220	0.0219	0.0218	0.0216	0.0214	0.0212	0.0210	0.0192
ln [*cis* + *trans*]		-3.8130	-3.8152	-3.8192	-3.8237	-3.8334	-3.8454	-3.8538	-3.8650	-3.9509

Table B.23 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 70°C

6-2 Methane sulfonic acid	time (sec)	0	1354	5304	9256	13202	17152	21102	25049	28993	32936	36888
	% 2,6-*trans*	0	3.5	9.4	14.3	18.5	22.1	25.2	28.0	30.3	32.4	34.2
area Naphthalene			549.8	546.7	545.6	543.7	547.2	546.6	545.5	548.5	550.6	548.8
area 2,6-*cis*			898.4	834.5	783.8	742.0	709.0	678.3	649.3	626.8	610.1	591.4
area 2,6-*trans*			32.7	86.4	130.6	168.2	201.0	228.8	251.9	272.6	292.3	307.6
Conc. 2,6-*cis*	(mol/L)		0.0222	0.0207	0.0195	0.0185	0.0176	0.0169	0.0162	0.0155	0.0150	0.0146
Conc. 2,6-*trans*	(mol/L)		0.0008	0.0021	0.0033	0.0042	0.0050	0.0057	0.0063	0.0067	0.0072	0.0076
ln [*trans* eq/*trans* eq-*trans* x]			0.0725	0.2069	0.3348	0.4591	0.5798	0.6981	0.8137	0.9258	1.0363	1.1444
ln [*cis-cis* eq]			-4.5341	-4.6738	-4.8068	-4.9322	-5.0596	-5.1799	-5.3001	-5.4196	-5.5307	-5.6393
cis + *trans*	(mol/L)		0.0230	0.0229	0.0228	0.0227	0.0226	0.0225	0.0224	0.0223	0.0223	0.0222
ln [*cis* + *trans*]			-3.7724	-3.7778	-3.7829	-3.7840	-3.7906	-3.7927	-3.7972	-3.8047	-3.8052	-3.8057

6-2 Methane sulfonic acid	time (sec)	40845	44805	48759	52710	56659	60607	64553	68497	72446	76393	176052
	% 2,6-*trans*	35.8	37.3	38.6	39.7	40.8	41.7	42.5	43.2	43.9	44.5	49.8
area Naphthalene		551.3	553.6	555.8	554.1	554.2	554.5	555.4	558.4	556.8	558.1	627.3
area 2,6-*cis*		576.2	563.5	551.3	539.1	528.8	516.2	511.7	504.3	496.8	491.2	453.2
area 2,6-*trans*		321.7	335.5	345.9	355.6	363.8	368.6	377.7	384.2	388.8	393.8	449.1
Conc. 2,6-*cis*	(mol/L)	0.0142	0.0138	0.0135	0.0132	0.0130	0.0126	0.0125	0.0123	0.0121	0.0120	0.0098
Conc. 2,6-*trans*	(mol/L)	0.0079	0.0082	0.0085	0.0087	0.0089	0.0090	0.0092	0.0093	0.0095	0.0096	0.0097
ln [*trans* eq/*trans* eq-*trans* x]		1.2507	1.3603	1.4610	1.5690	1.6708	1.7712	1.8705	1.9760	2.0759	2.1751	4.7665
ln [*cis-cis* eq]		-5.7513	-5.8638	-5.9705	-6.0782	-6.1826	-6.2922	-6.3880	-6.5000	-6.6002	-6.7024	-9.3914
cis + *trans*	(mol/L)	0.0221	0.0221	0.0219	0.0219	0.0219	0.0217	0.0217	0.0216	0.0216	0.0215	0.0195
ln [*cis* + *trans*]		-3.8115	-3.8144	-3.8204	-3.8201	-3.8226	-3.8319	-3.8284	-3.8348	-3.8352	-3.8382	-3.9357

Table B.24 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 17 mM methanesulphonic acid in nitromethane at 70°C

6-3 Methane sulfonic acid	time (sec)	0	2670	6621	10583	14518	18470	22419	26363	30308	34252	38207
	% 2,6-*trans*	0	4.3	8.5	12.1	15.4	18.3	21.0	23.3	25.5	27.4	29.2
area Naphthalene			542.7	543.3	546.9	543.8	550.3	544.3	549.3	558.0	555.2	563.5
area 2,6-*cis*			879.0	837.3	807.8	768.1	749.4	715.3	700.1	685.7	663.7	656.3
area 2,6-*trans*			39.3	77.4	111.6	139.9	168.1	189.8	212.9	234.2	250.8	270.9
Conc. 2,6-*cis*	(mol/L)		0.0220	0.0209	0.0201	0.0192	0.0185	0.0178	0.0173	0.0167	0.0162	0.0158
Conc. 2,6-*trans*	(mol/L)		0.0010	0.0019	0.0028	0.0035	0.0041	0.0047	0.0053	0.0057	0.0061	0.0065
ln [*trans* eq/*trans* eq-*trans* x]			0.0891	0.1846	0.2768	0.3666	0.4541	0.5408	0.6246	0.7076	0.7903	0.8723
ln [*cis-cis* eq]			-4.5515	-4.6521	-4.7457	-4.8423	-4.9313	-5.0207	-5.1049	-5.1960	-5.2797	-5.3627
cis + *trans*	(mol/L)		0.0230	0.0229	0.0228	0.0227	0.0226	0.0226	0.0226	0.0224	0.0224	0.0223
ln [*cis* + *trans*]			-3.7733	-3.7783	-3.7798	-3.7866	-3.7880	-3.7907	-3.7911	-3.7993	-3.8002	-3.8012

6-3 Methane sulfonic acid	time (sec)	46122	50077	54027	57975	61921	65868	69813	73762	77709	102433	165538
	% 2,6-*trans*	32.4	33.8	35.0	36.1	37.2	38.1	39.0	39.8	40.6	44.2	48.6
area Naphthalene		566.9	564.8	566.0	566.2	566.7	568.6	571.7	570.8	572.8	581.5	754.7
area 2,6-*cis*		624.9	610.0	599.2	587.5	575.2	567.7	561.1	551.5	545.9	509.9	575.6
area 2,6-*trans*		299.3	310.8	322.6	332.3	340.4	349.9	359.0	365.1	372.8	403.3	544.3
Conc. 2,6-*cis*	(mol/L)	0.0150	0.0147	0.0144	0.0141	0.0138	0.0136	0.0133	0.0131	0.0129	0.0119	0.0104
Conc. 2,6-*trans*	(mol/L)	0.0072	0.0075	0.0077	0.0080	0.0082	0.0084	0.0085	0.0087	0.0088	0.0094	0.0098
ln [*trans* eq/*trans* eq-*trans* x]		1.0360	1.1159	1.1945	1.2718	1.3494	1.4255	1.5017	1.5773	1.6521	2.1182	3.4476
ln [*cis-cis* eq]		-5.5356	-5.6155	-5.6952	-5.7750	-5.8580	-5.9353	-6.0142	-6.0920	-6.1680	-6.6552	-8.0413
cis + *trans*	(mol/L)	0.0221	0.0221	0.0221	0.0221	0.0219	0.0219	0.0219	0.0218	0.0218	0.0213	0.0201
ln [*cis* + *trans*]		-3.8105	-3.8105	-3.8115	-3.8140	-3.8195	-3.8207	-3.8234	-3.8256	-3.8268	-3.8479	-3.9046

Table B.25 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 15 mM methanesulphonic acid in nitromethane at 70°C

7-1 Methane sulfonic acid	time (sec)	0	326	2954	5588	8223	10855	13492	16126	18759
	% 2,6-*trans*	0	1.6	8.7	14.6	19.5	23.7	27.2	30.2	32.8
area Naphthalene			548.2	553.7	549.2	548.4	552.2	549.3	551.6	551.3
area 2,6-*cis*			920.5	850.3	789.4	741.3	702.8	664.1	629.5	609.8
area 2,6-*trans*			14.7	81.2	134.9	179.8	218.0	247.5	272.4	297.1
Conc. 2,6-*cis*	(mol/L)		0.0228	0.0209	0.0195	0.0184	0.0173	0.0164	0.0155	0.0150
Conc. 2,6-*trans*	(mol/L)		0.0004	0.0020	0.0033	0.0045	0.0054	0.0061	0.0067	0.0073
ln [*trans* eq/*trans* eq-*trans* x]			0.0318	0.1907	0.3435	0.4924	0.6379	0.7784	0.9204	1.0572
ln [*cis*-*cis* eq]			-4.4861	-4.6590	-4.8113	-4.9622	-5.1150	-5.2602	-5.4171	-5.5479
cis + *trans*	(mol/L)		0.0232	0.0228	0.0229	0.0228	0.0226	0.0225	0.0222	0.0223
ln [*cis* + *trans*]			-3.7651	-3.7791	-3.7787	-3.7807	-3.7879	-3.7927	-3.8076	-3.8015

7-1 Methane sulfonic acid	time (sec)	21392	24026	29293	34555	39818	45081	52970	68778	84556
	% 2,6-*trans*	35.0	36.9	39.9	42.3	44.0	45.4	46.8	48.5	49.4
area Naphthalene		554.5	556.3	555.7	555.8	553.0	548.6	555.2	553.4	553.1
area 2,6-*cis*		584.2	569.2	534.6	510.8	490.5	474.8	459.0	434.5	418.8
area 2,6-*trans*		314.3	332.3	355.2	373.8	385.7	394.2	404.2	409.4	408.2
Conc. 2,6-*cis*	(mol/L)	0.0143	0.0139	0.0131	0.0125	0.0120	0.0118	0.0112	0.0107	0.0103
Conc. 2,6-*trans*	(mol/L)	0.0077	0.0081	0.0087	0.0091	0.0095	0.0098	0.0099	0.0100	0.0100
ln [*trans* eq/*trans* eq-*trans* x]		1.1934	1.3253	1.5857	1.8436	2.0946	2.3396	2.6998	3.3930	4.0893
ln [*cis*-*cis* eq]		-5.6992	-5.8309	-6.1033	-6.3673	-6.6228	-6.8680	-7.2469	-7.9594	-8.6755
cis + *trans*	(mol/L)	0.0220	0.0220	0.0217	0.0216	0.0215	0.0215	0.0211	0.0207	0.0203
ln [*cis* + *trans*]		-3.8166	-3.8165	-3.8285	-3.8345	-3.8390	-3.8393	-3.8579	-3.8773	-3.8970

Table B.26 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 22 mM methanesulphonic acid in nitromethane at 70°C

7-2 Methane sulfonic acid	time (sec)	0	1638	4270	6905	9539	12174	14810	17444	20075
	% 2,6-*trans*	0	7.8	16.9	24.0	29.4	33.6	36.9	39.5	41.6
area Naphthalene			545.3	546.4	545.1	543.9	553.1	542.7	551.1	544.0
area 2,6-*cis*			853.6	762.6	691.3	636.7	598.4	561.0	535.3	514.5
area 2,6-*trans*			71.9	155.5	217.9	264.6	303.0	328.0	349.5	365.8
Conc. 2,6-*cis*	(mol/L)		0.0213	0.0190	0.0172	0.0159	0.0147	0.0140	0.0132	0.0128
Conc. 2,6-*trans*	(mol/L)		0.0018	0.0039	0.0054	0.0066	0.0074	0.0082	0.0086	0.0091
ln [*trans* eq/*trans* eq-*trans* x]			0.1681	0.4116	0.6490	0.8790	1.1075	1.3279	1.5458	1.7589
ln [*cis*-*cis* eq]			-4.6275	-4.8810	-5.1258	-5.3623	-5.6075	-5.8228	-6.0608	-6.2660
cis + *trans*	(mol/L)		0.0230	0.0228	0.0226	0.0225	0.0221	0.0222	0.0218	0.0220
ln [*cis* + *trans*]			-3.7702	-3.7803	-3.7876	-3.7942	-3.8108	-3.8057	-3.8258	-3.8179

7-2 Methane sulfonic acid	time (sec)	22710	25343	30608	35871	41134	46397	54285	70095	85870
	% 2,6-*trans*	43.2	44.5	46.4	47.7	48.5	49.0	49.6	50.0	50.2
area Naphthalene		548.5	551.8	550.2	542.6	548.0	545.1	550.7	538.2	547.9
area 2,6-*cis*		499.0	484.5	462.7	446.6	433.9	428.0	416.3	397.7	388.9
area 2,6-*trans*		379.4	388.8	401.2	407.1	409.0	411.7	409.6	398.2	391.8
Conc. 2,6-*cis*	(mol/L)	0.0124	0.0119	0.0114	0.0112	0.0108	0.0107	0.0103	0.0100	0.0096
Conc. 2,6-*trans*	(mol/L)	0.0094	0.0096	0.0099	0.0102	0.0101	0.0103	0.0101	0.0100	0.0097
ln [*trans* eq/*trans* eq-*trans* x]		1.9690	2.1792	2.5917	2.9944	3.3990	3.7585	4.4175	5.6963	8.1657
ln [*cis*-*cis* eq]		-6.4865	-6.7085	-7.1290	-7.5295	-7.9568	-8.3148	-9.0006	-10.2935	-12.8000
cis + *trans*	(mol/L)	0.0217	0.0215	0.0213	0.0214	0.0209	0.0209	0.0204	0.0201	0.0193
ln [*cis* + *trans*]		-3.8283	-3.8401	-3.8481	-3.8460	-3.8687	-3.8672	-3.8940	-3.9080	-3.9451

Table B.27 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 27 mM methanesulphonic acid in nitromethane at 70°C

7-3 Methane sulfonic acid	time (sec)	0	42	1359	2674	3989	5304	6618	7933	9246
	% 2,6-*trans*	0	2.3	8.7	14.3	19.1	23.2	26.8	29.8	32.3
area Naphthalene			551.1	551.2	547.0	553.0	554.4	549.6	550.5	556.4
area 2,6-*cis*			910.2	843.9	784.1	737.1	699.7	664.4	630.7	612.3
area 2,6-*trans*			21.5	80.0	131.3	174.5	211.4	242.7	267.4	292.4
Conc. 2,6-*cis*	(mol/L)		0.0224	0.0208	0.0195	0.0181	0.0171	0.0164	0.0156	0.0149
Conc. 2,6-*trans*	(mol/L)		0.0005	0.0020	0.0033	0.0043	0.0052	0.0060	0.0066	0.0071
ln [*trans* eq/*trans* eq-*trans* x]			0.0471	0.1893	0.3365	0.4802	0.6203	0.7614	0.8992	1.0323
ln [*cis*-*cis* eq]			-4.5104	-4.6612	-4.8100	-4.9687	-5.1119	-5.2487	-5.3981	-5.5346
cis + *trans*	(mol/L)		0.0230	0.0228	0.0227	0.0224	0.0223	0.0224	0.0222	0.0221
ln [*cis* + *trans*]			-3.7741	-3.7827	-3.7843	-3.7994	-3.8025	-3.7982	-3.8098	-3.8131

Table B.28 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 29 mM methanesulphonic acid in nitromethane at 70°C

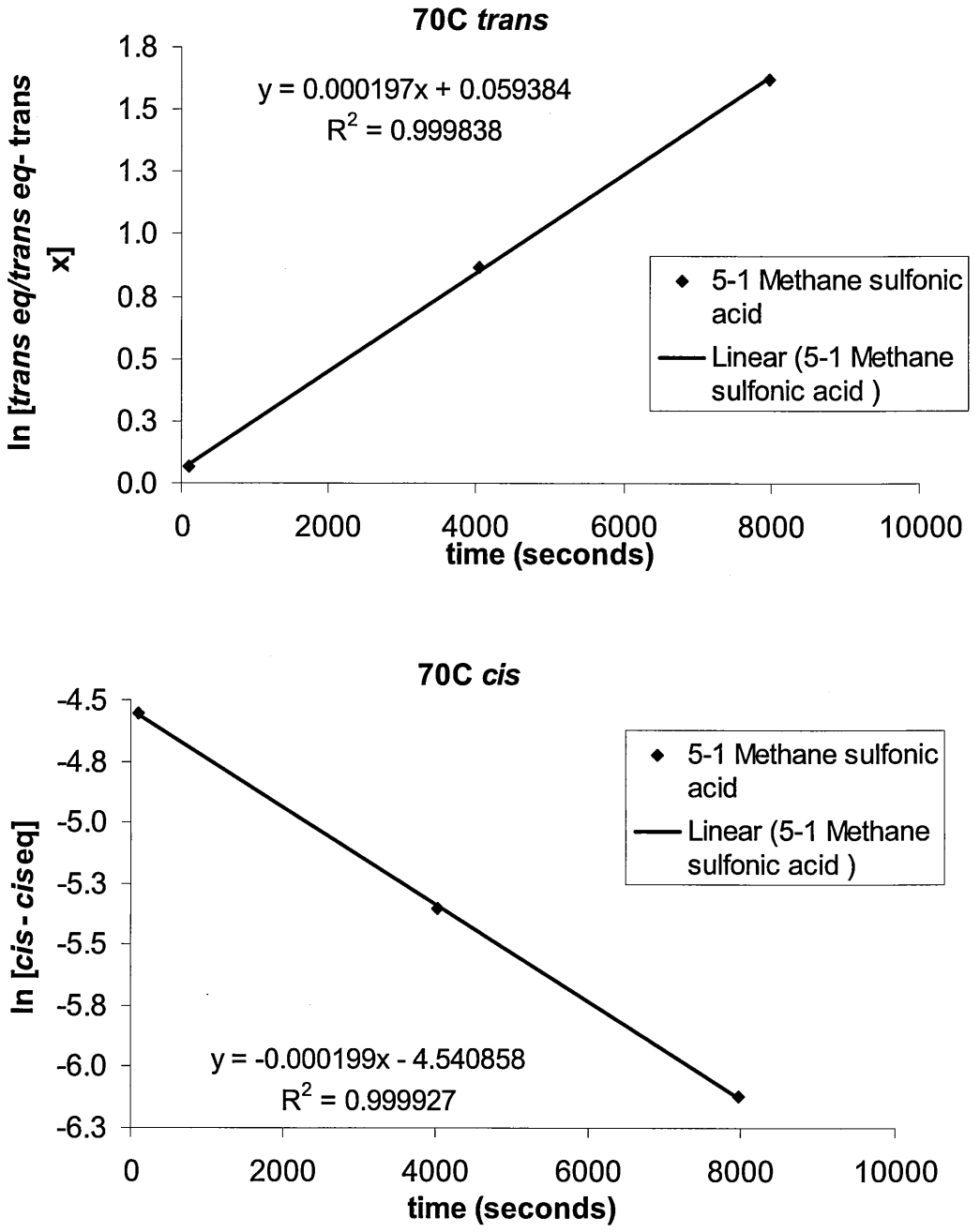


Figure B.20 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 36 mM methanesulphonic acid in nitromethane at 70°C

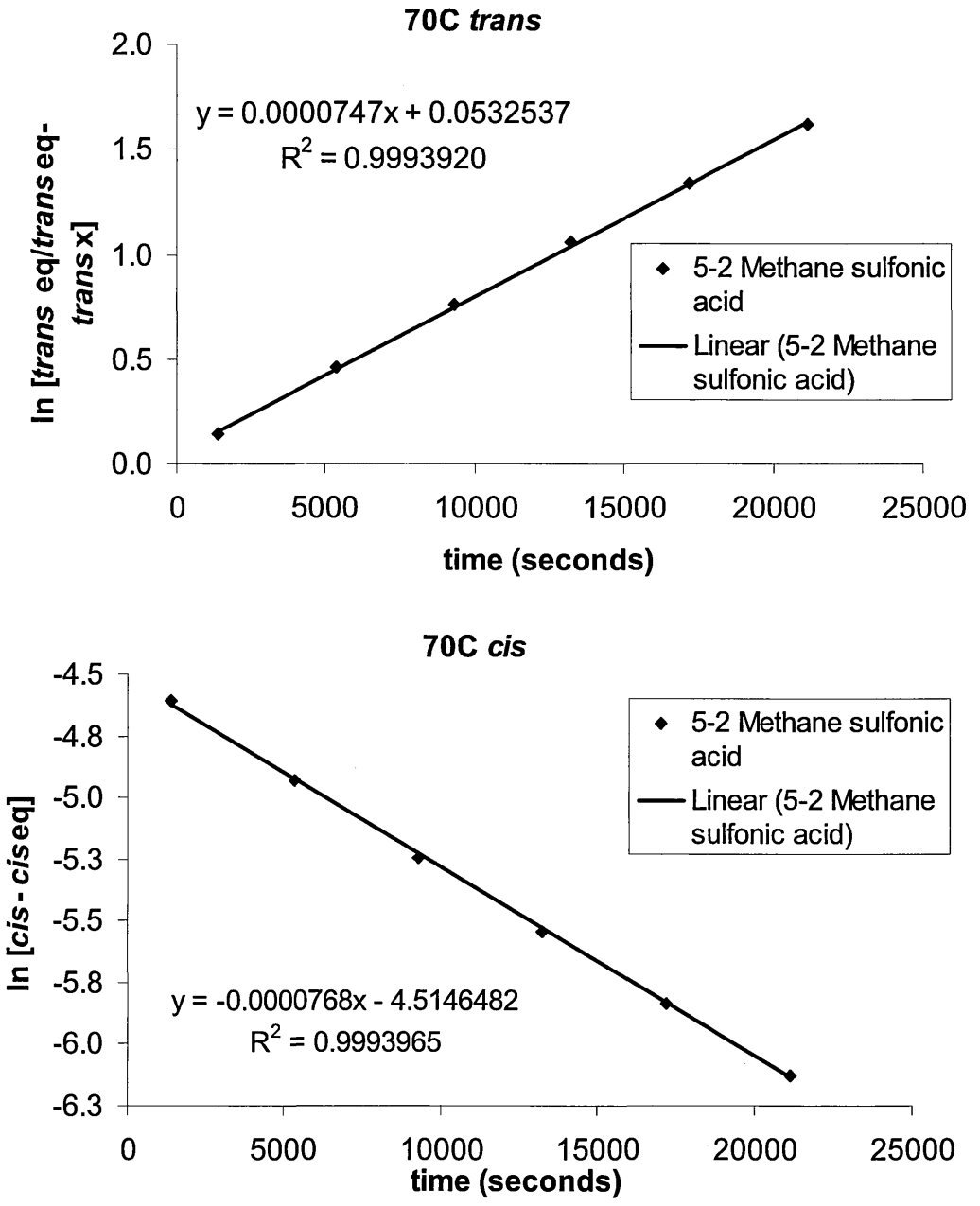


Figure B.21 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 70°C

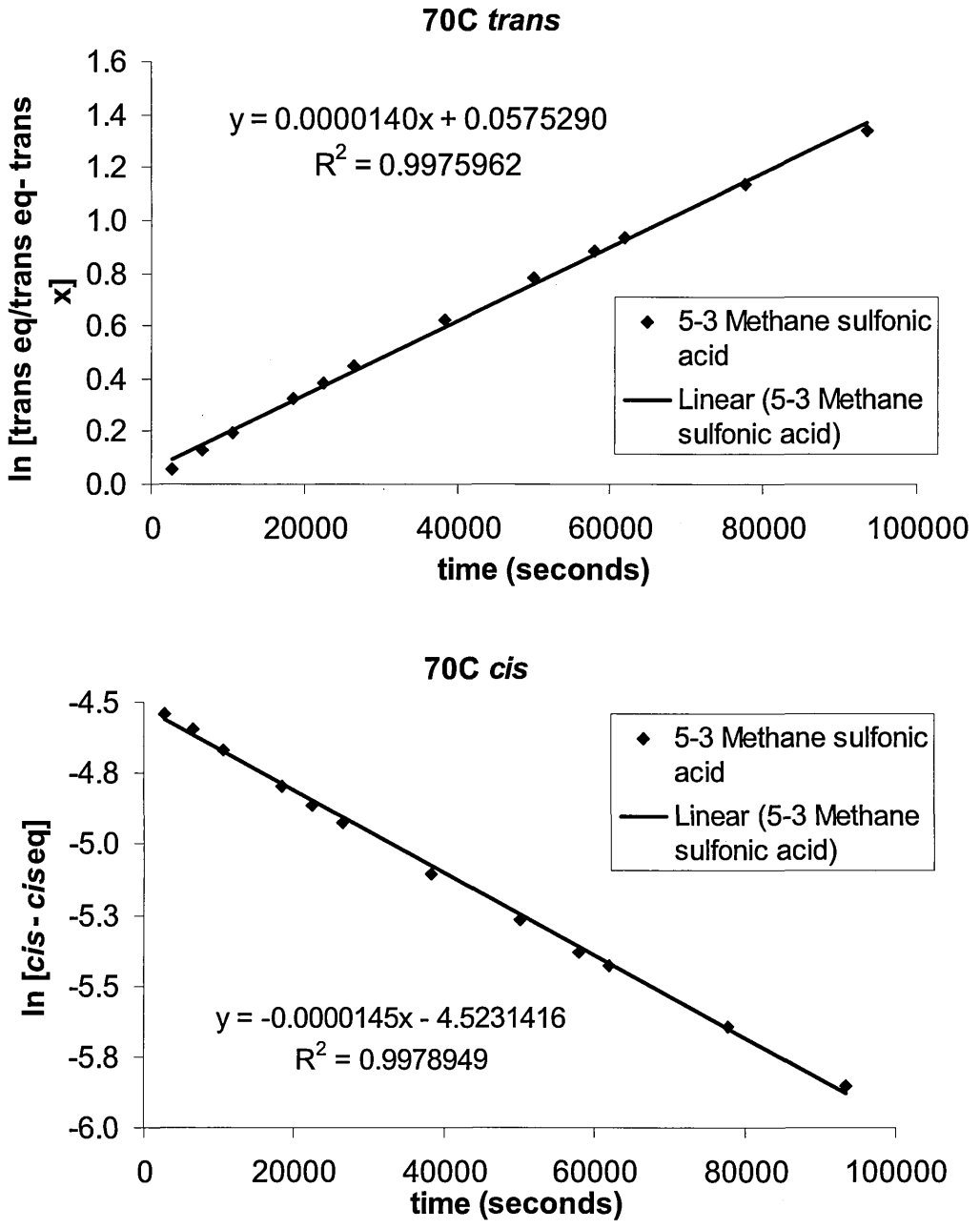


Figure B.22 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 12 mM methanesulphonic acid in nitromethane at 70°C

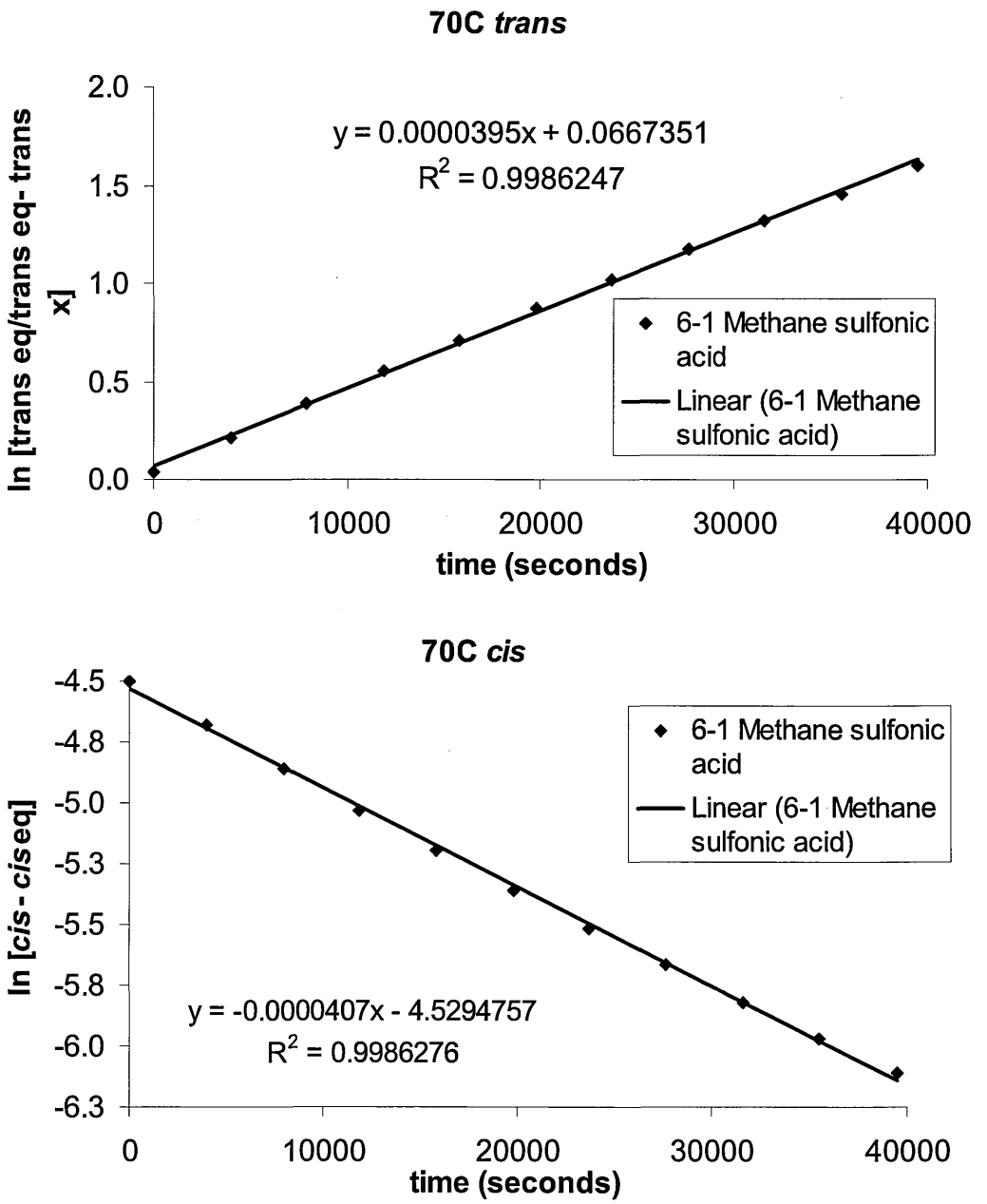


Figure B.23 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 70°C

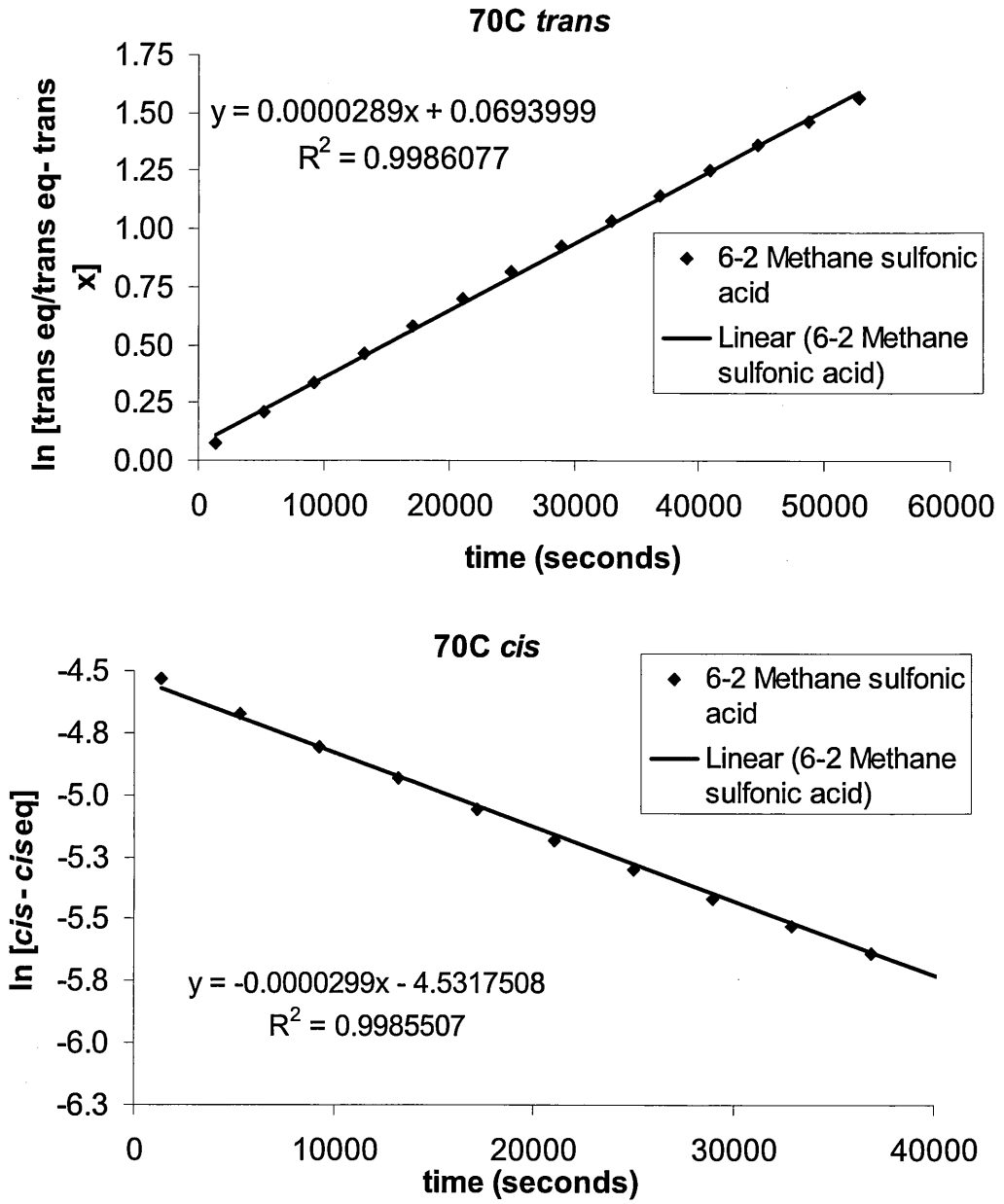


Figure B.24 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 17 mM methanesulphonic acid in nitromethane at 70°C

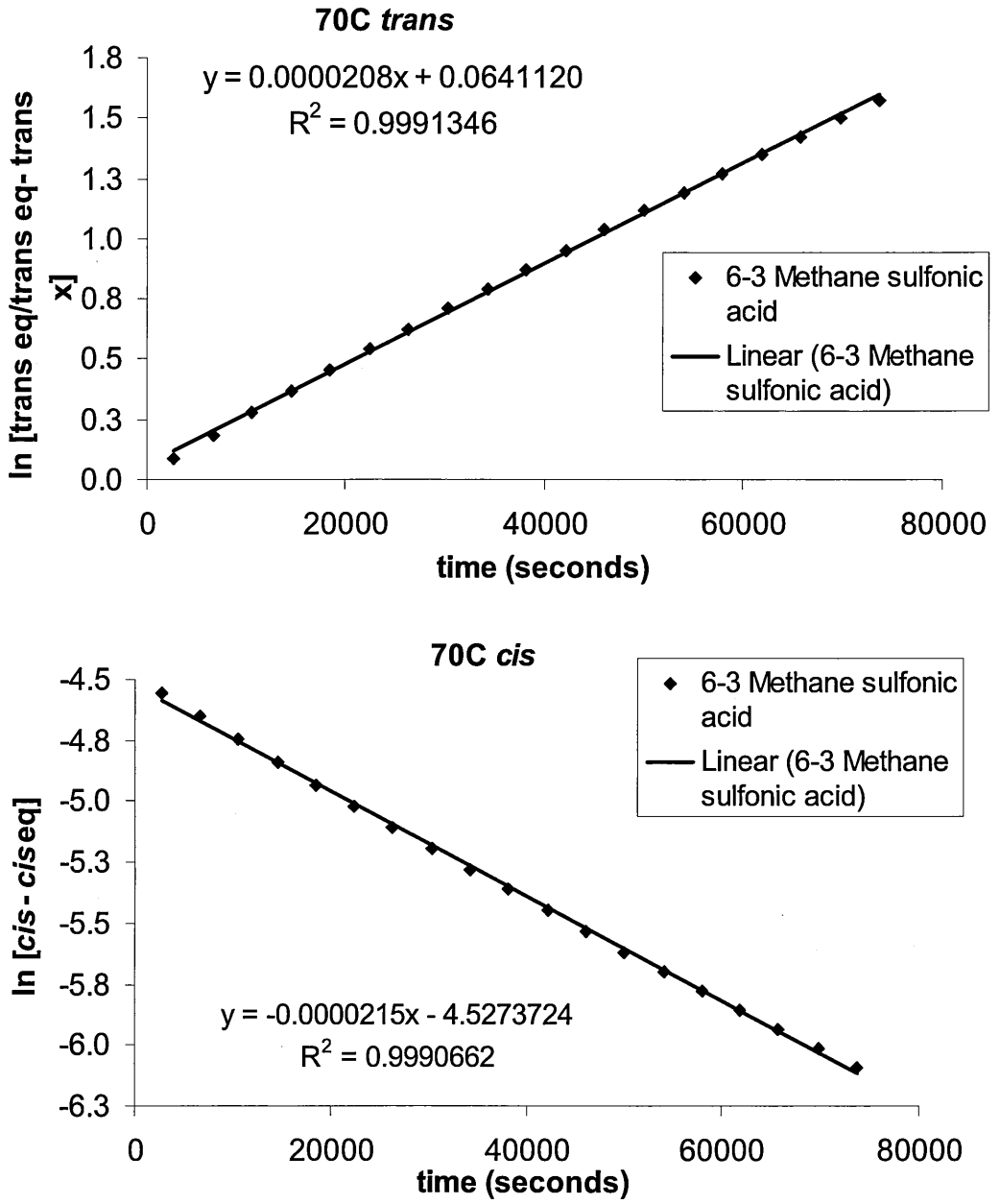


Figure B.25 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 15 mM methanesulphonic acid in nitromethane at 70°C

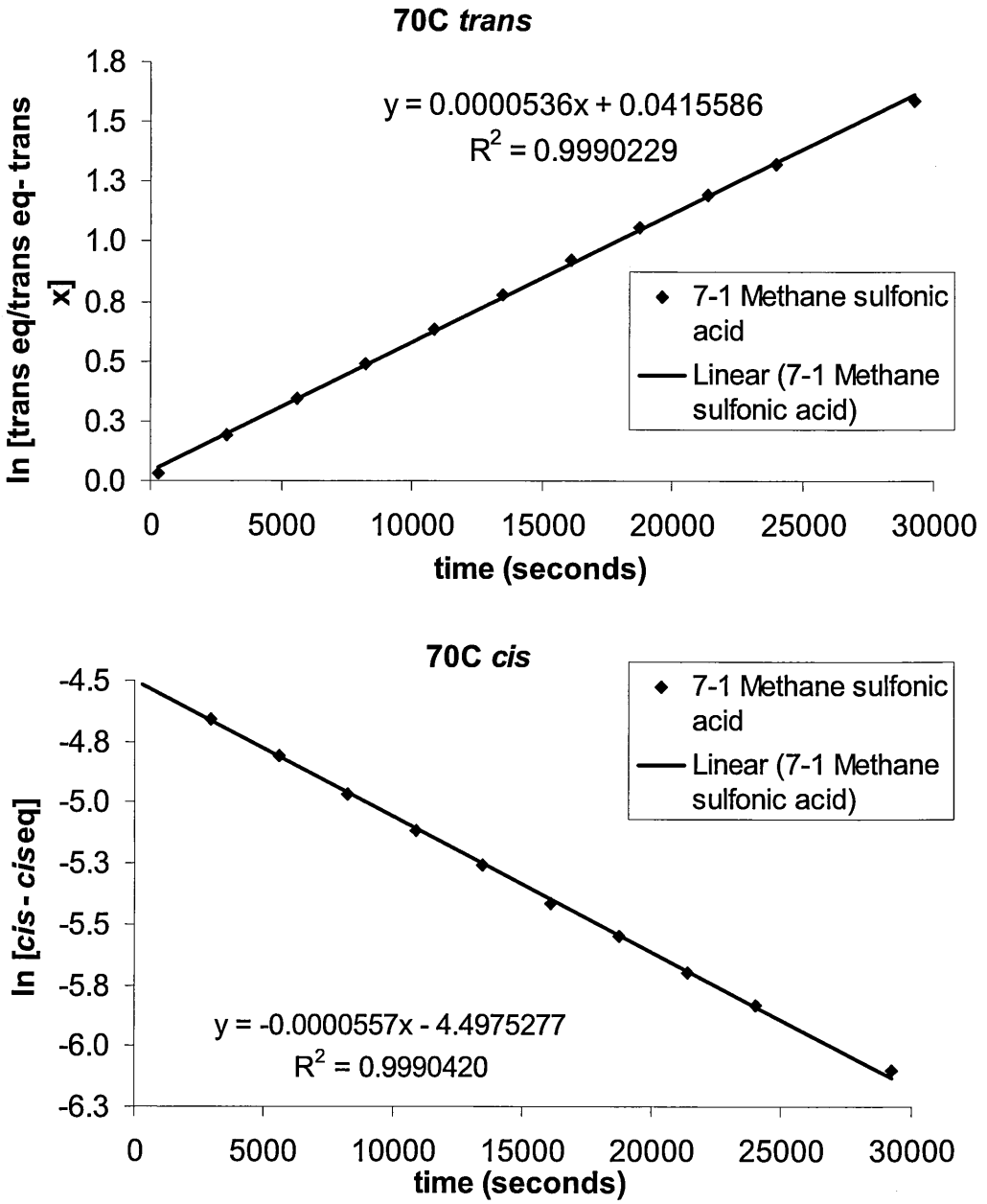


Figure B.26 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 22 mM methanesulphonic acid in nitromethane at 70°C

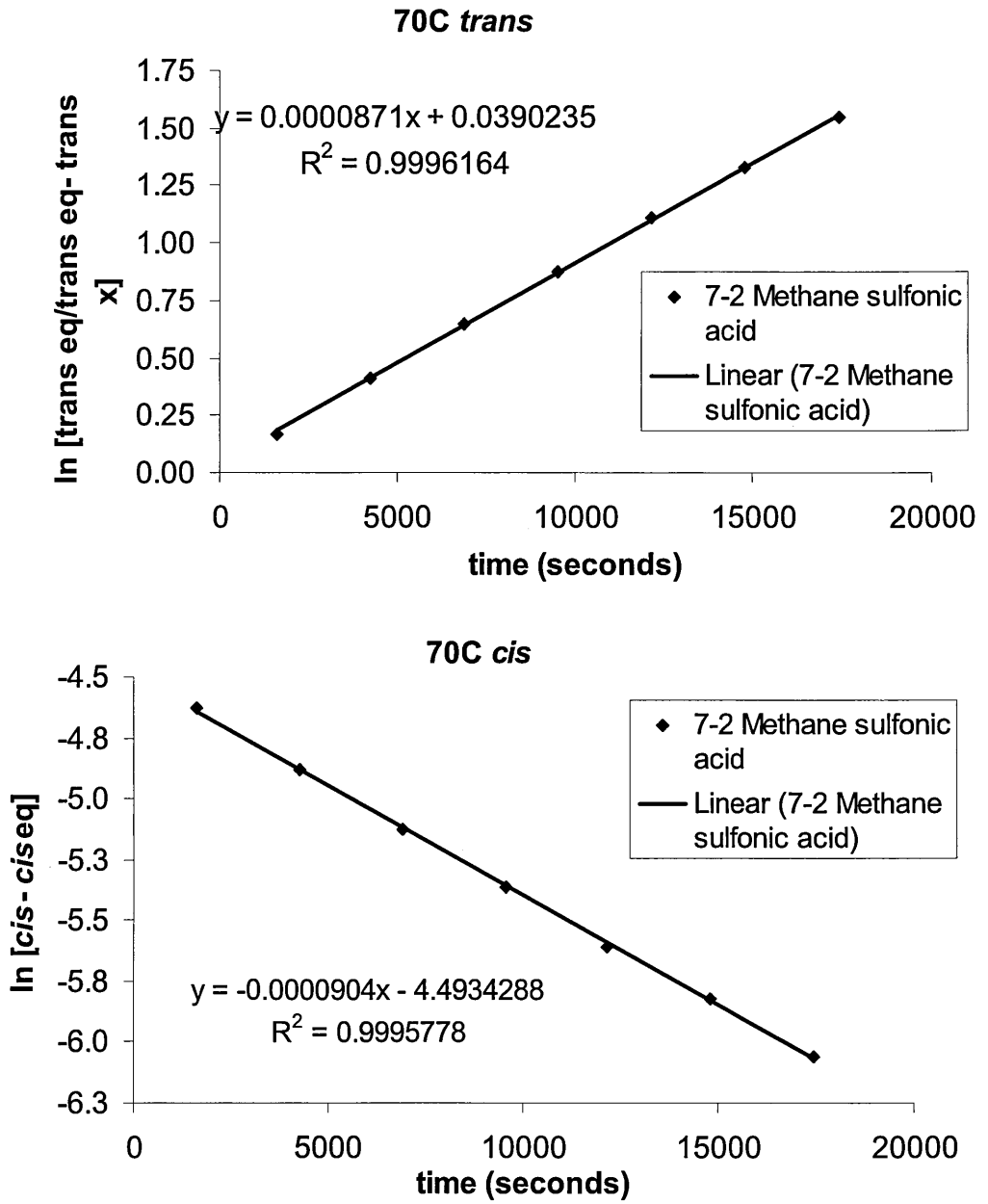


Figure B.27 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 27 mM methanesulphonic acid in nitromethane at 70°C

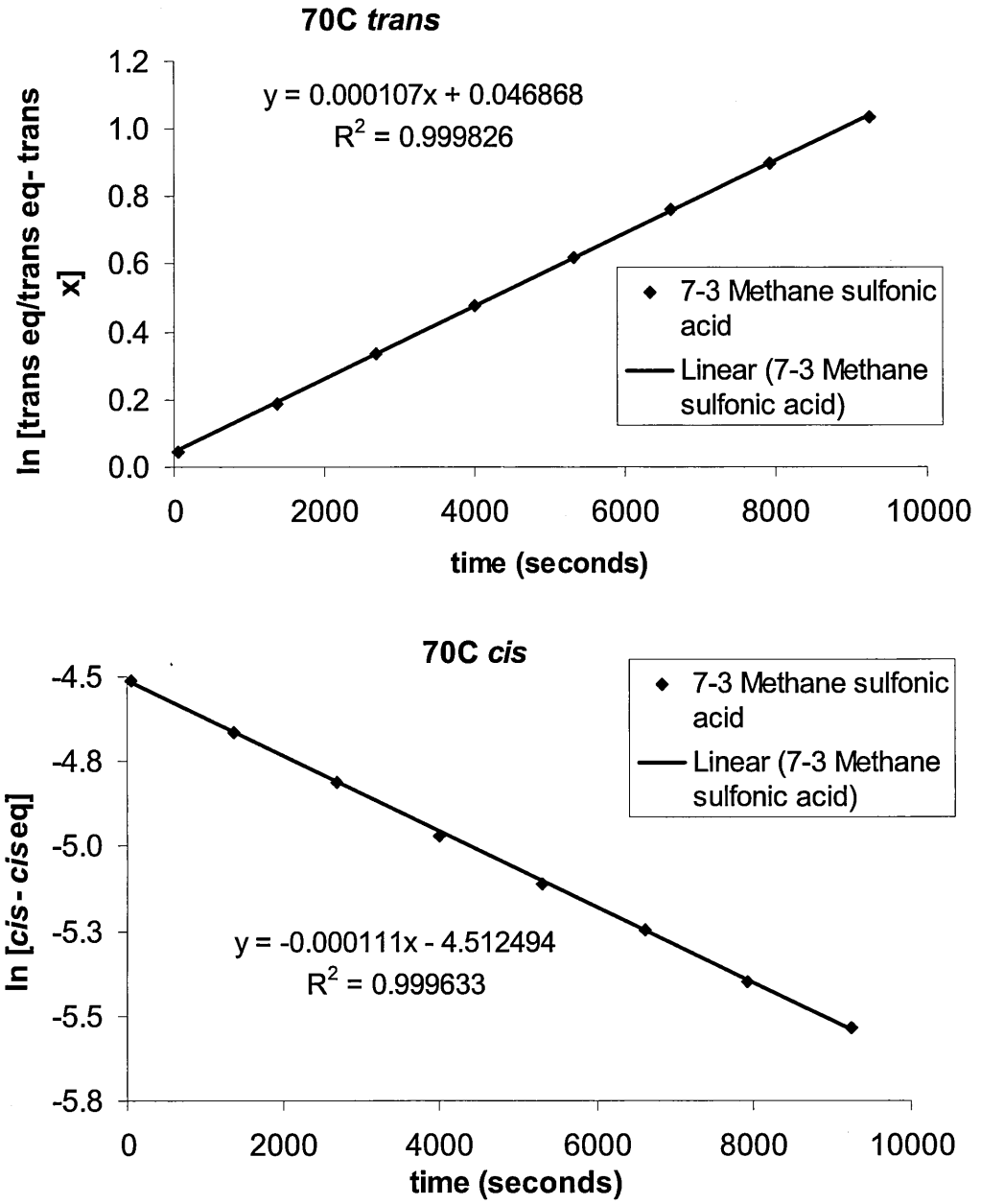


Figure B.28 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 29 mM methanesulphonic acid in nitromethane at 70°C

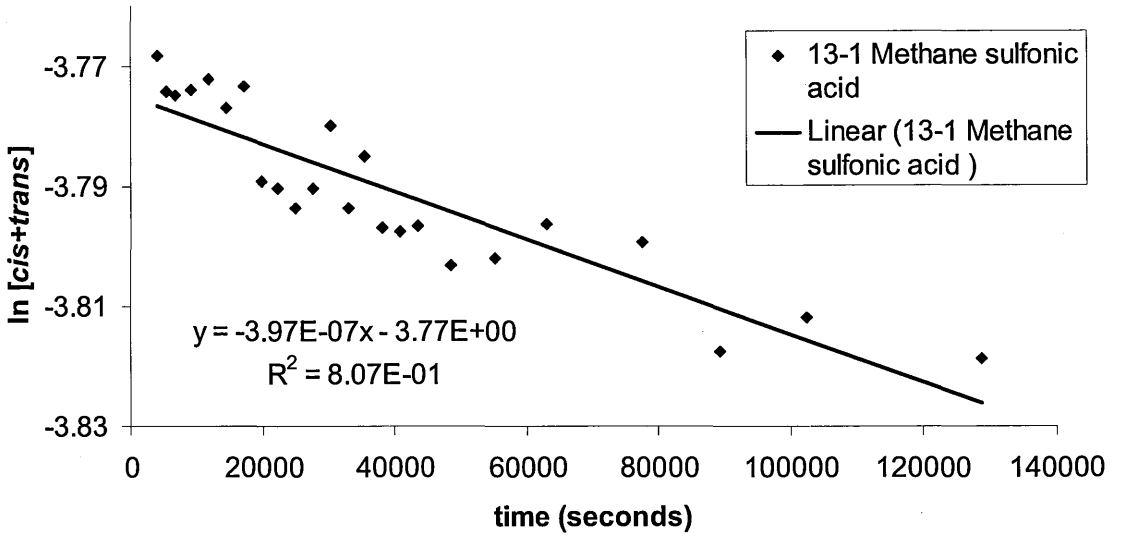


Figure B.29 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 40°C

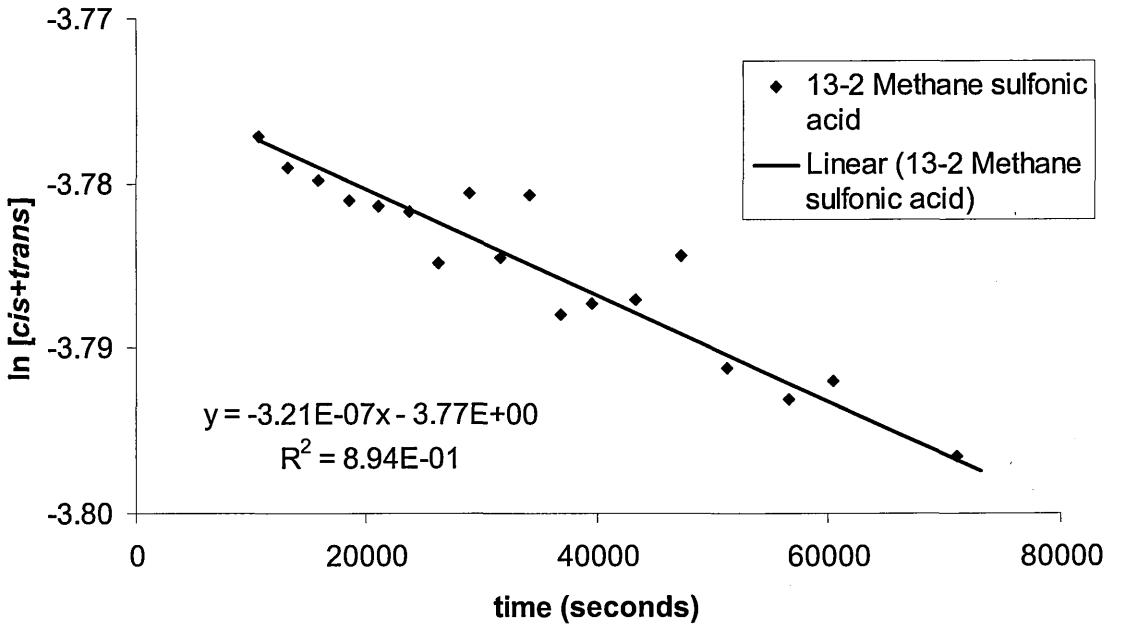


Figure B.30 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 23 mM methanesulphonic acid in nitromethane at 40°C

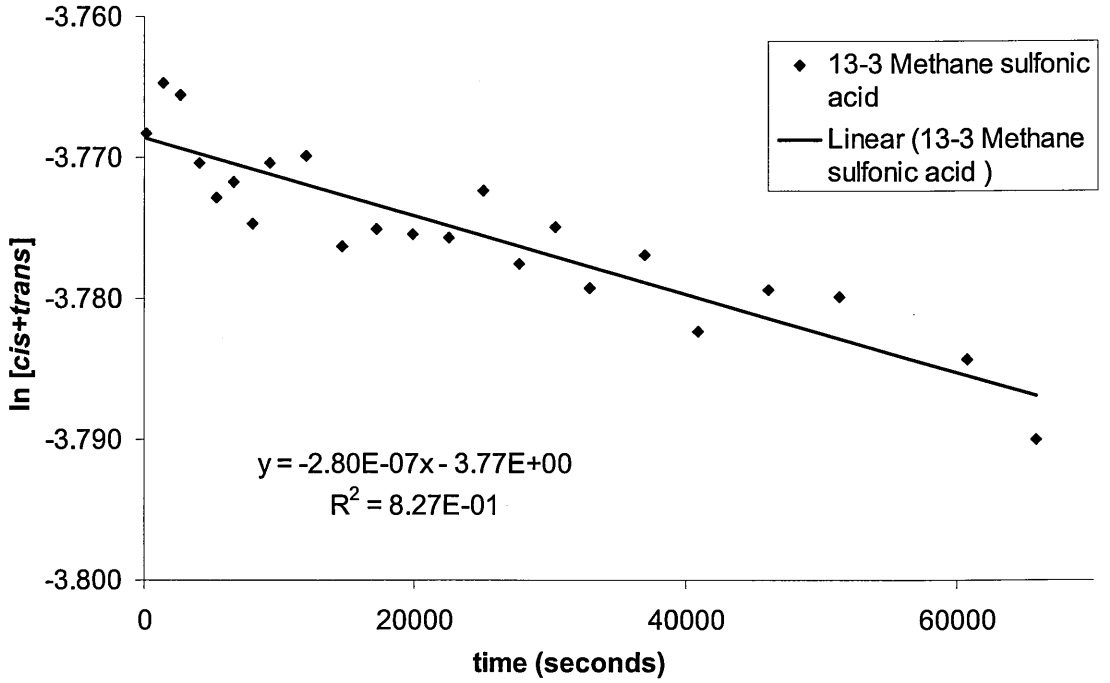


Figure B.31 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 21 mM methanesulphonic acid in nitromethane at 40°C

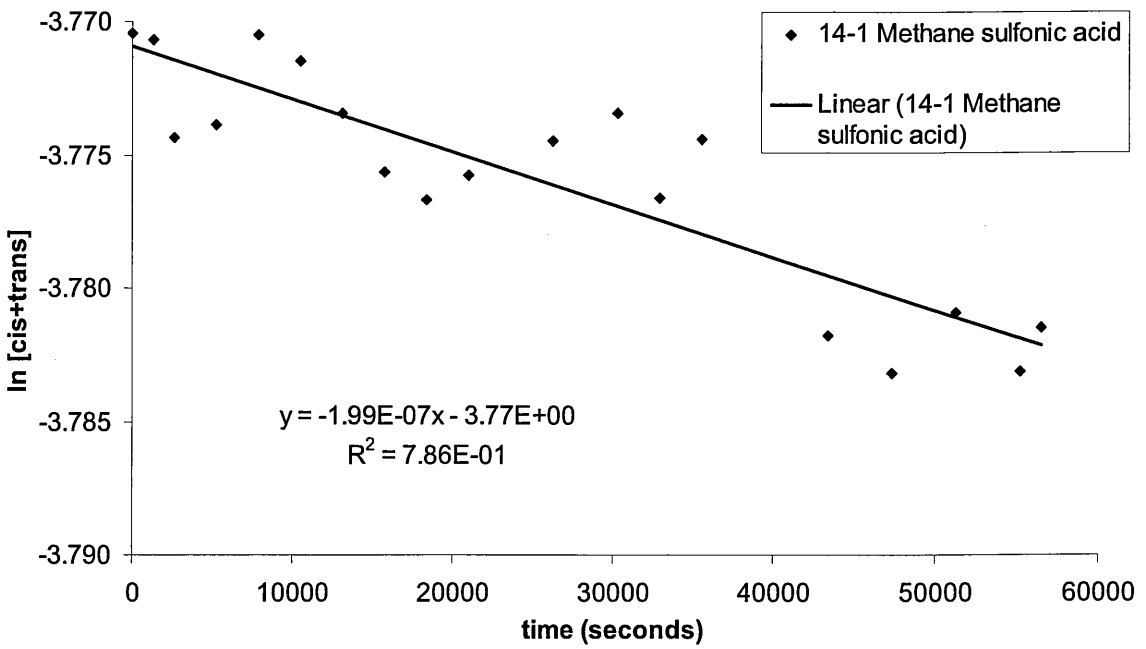


Figure B.32 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 40°C

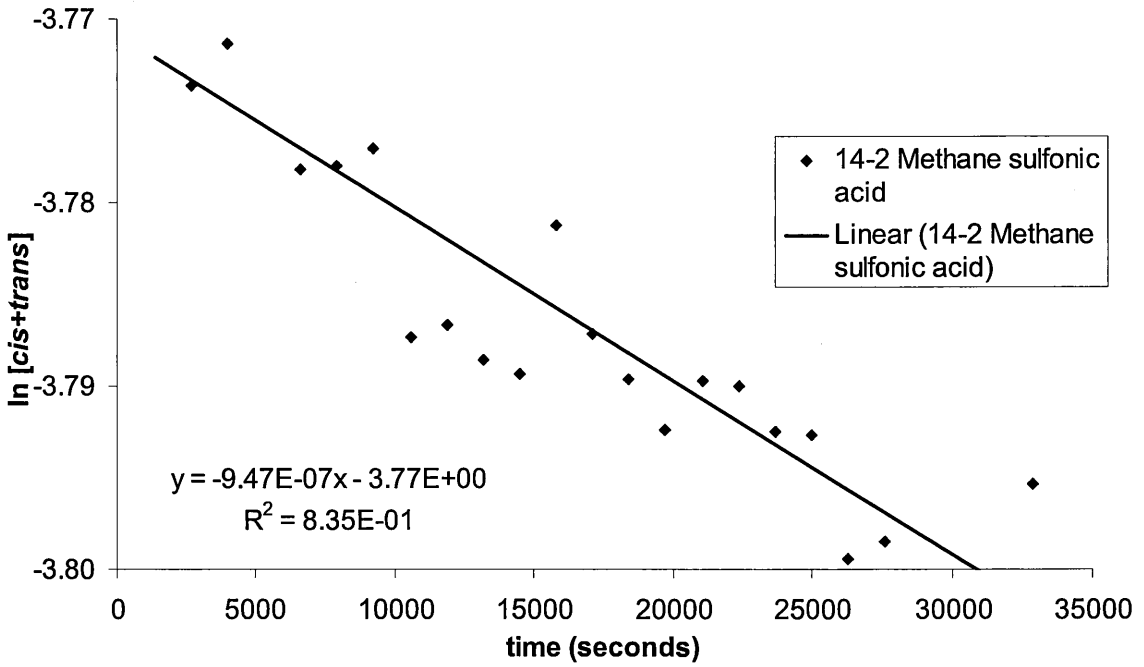


Figure B.33 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 26 mM methanesulphonic acid in nitromethane at 40°C

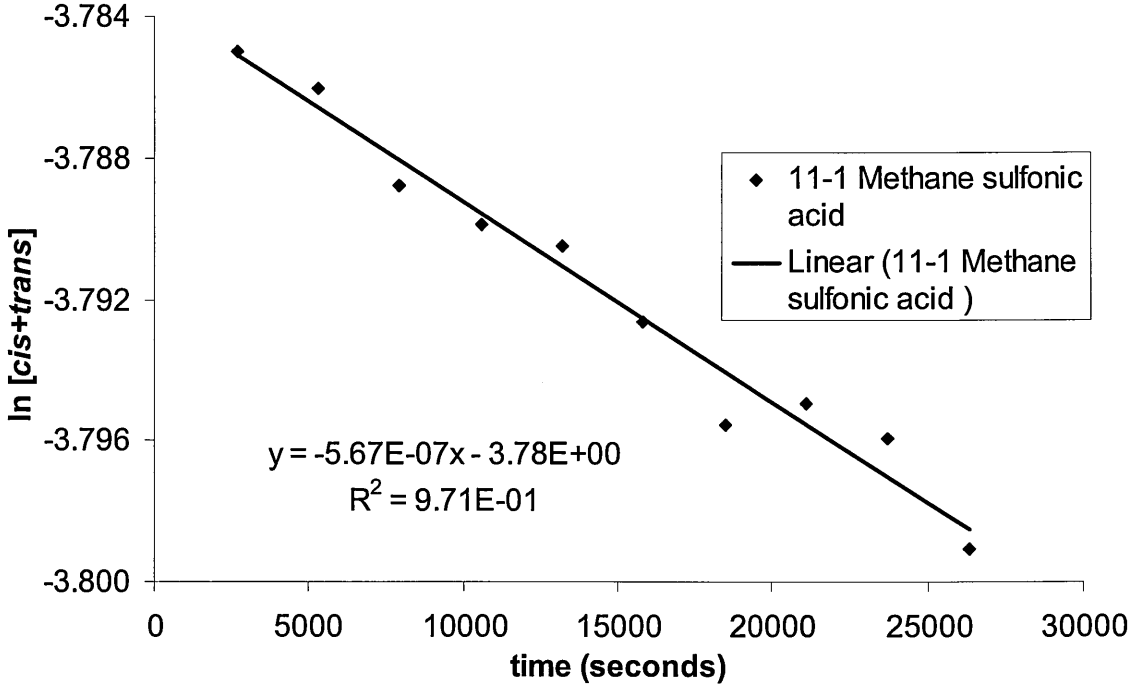


Figure B.34 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 50°C

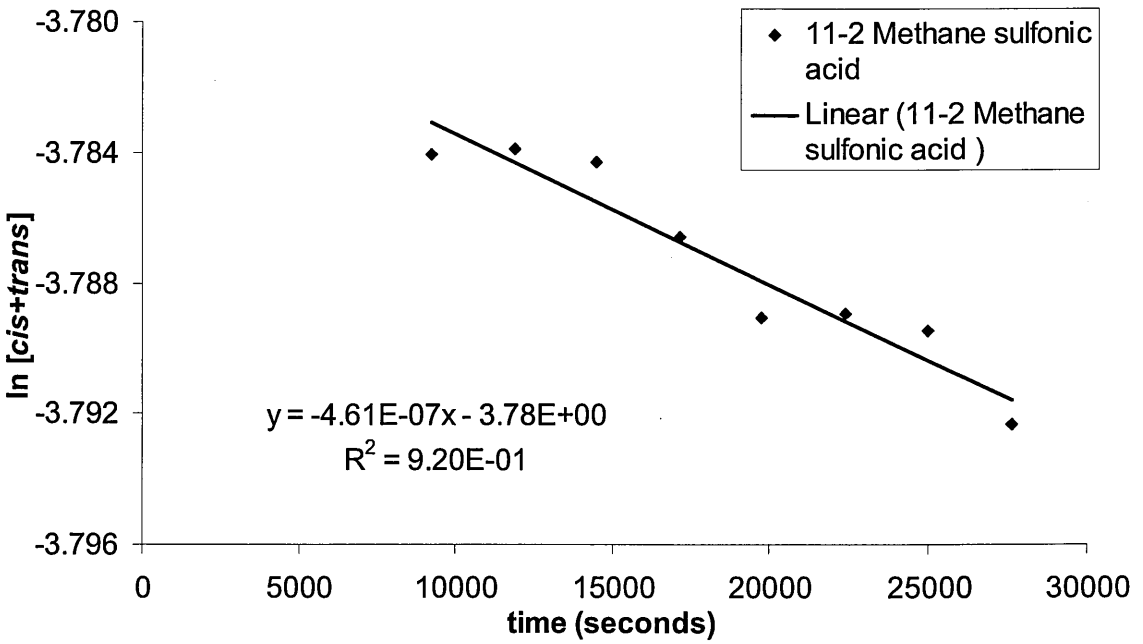


Figure B.35 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 22 mM methanesulphonic acid in nitromethane at 50°C

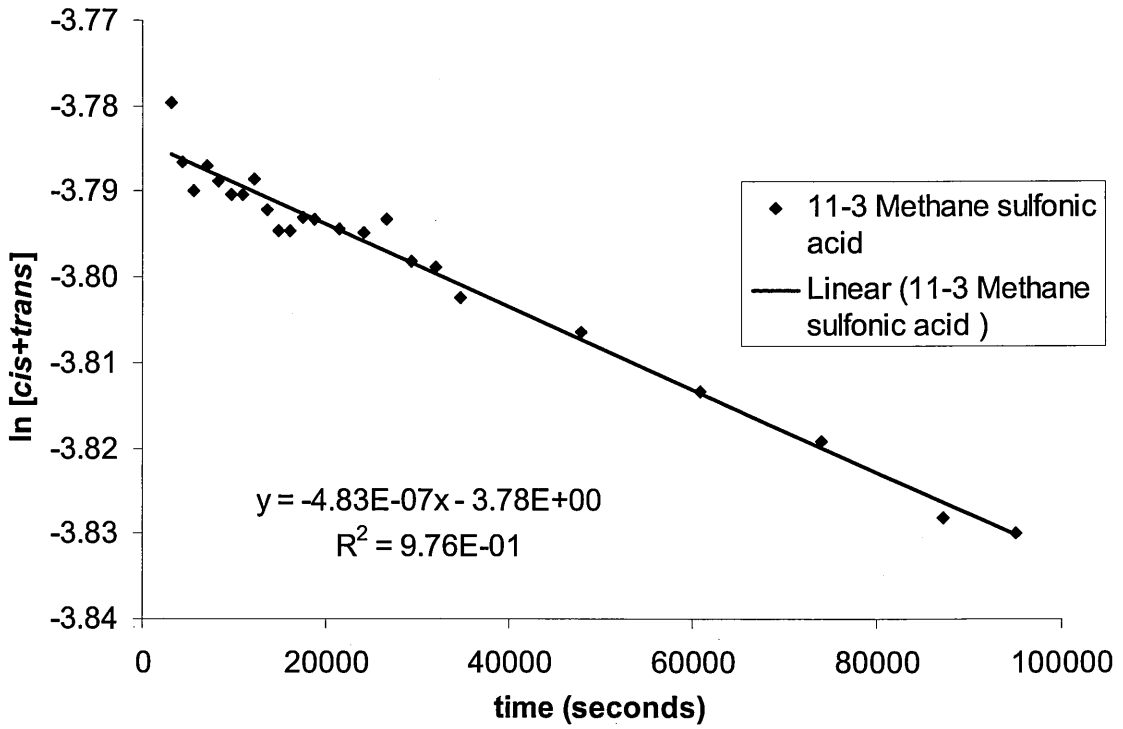


Figure B.36 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 50°C

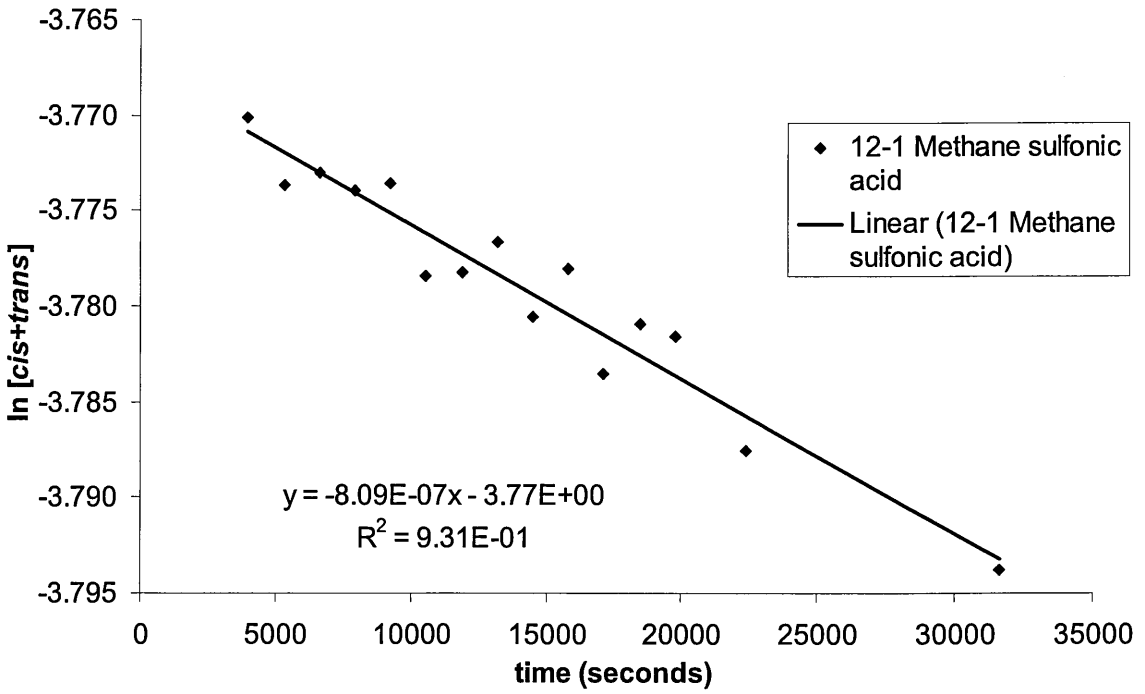


Figure B.37 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 27 mM methanesulphonic acid in nitromethane at 50°C

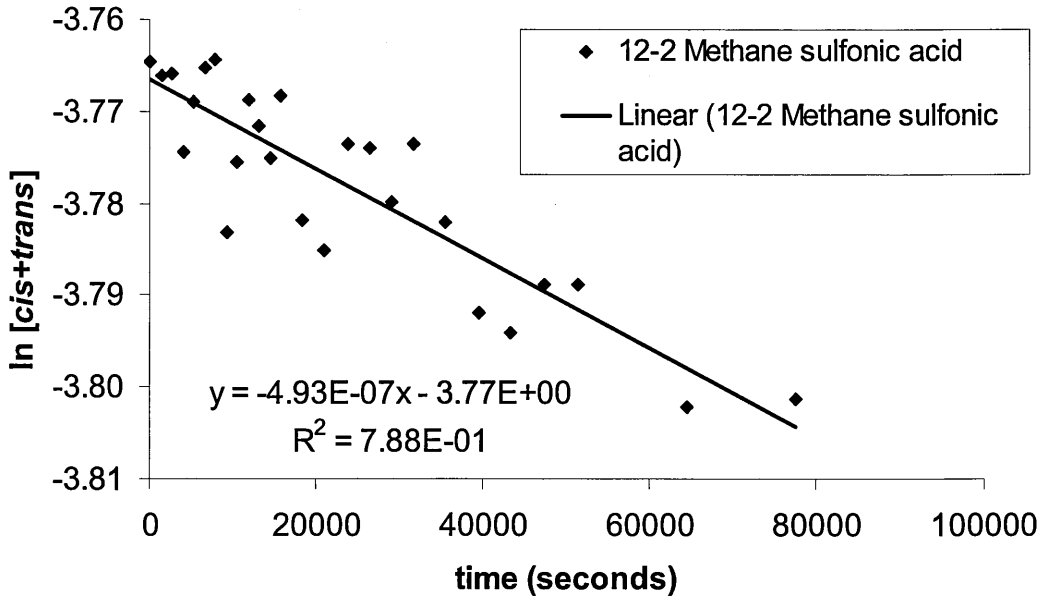


Figure B.38 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 50°C

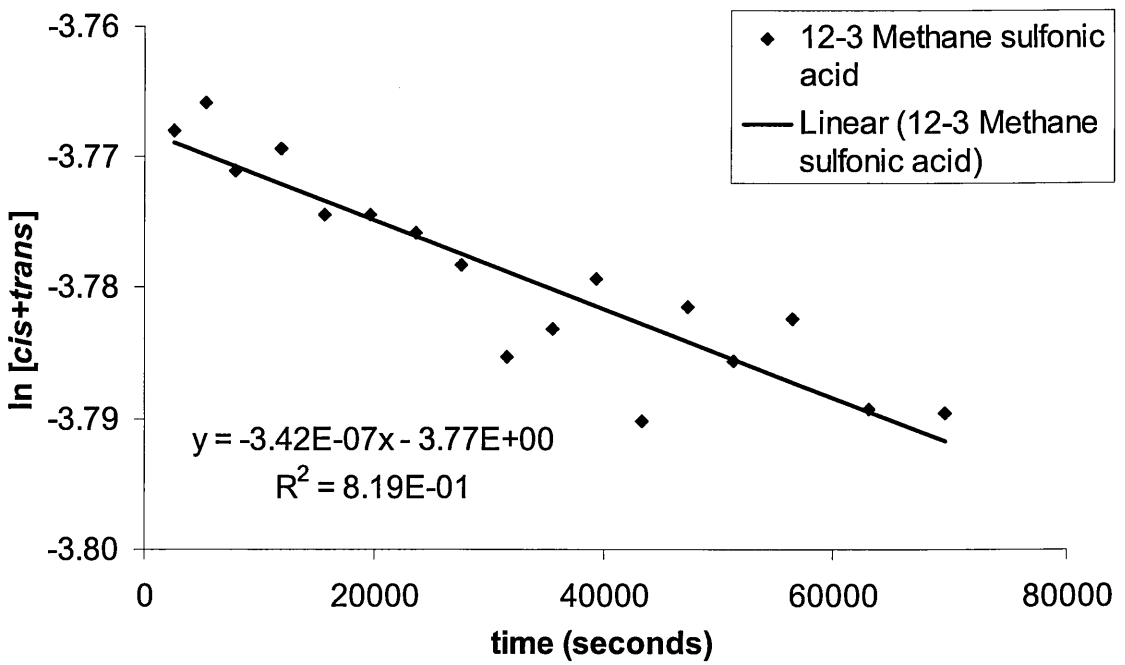


Figure B.39 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 16 mM methanesulphonic acid in nitromethane at 50°C

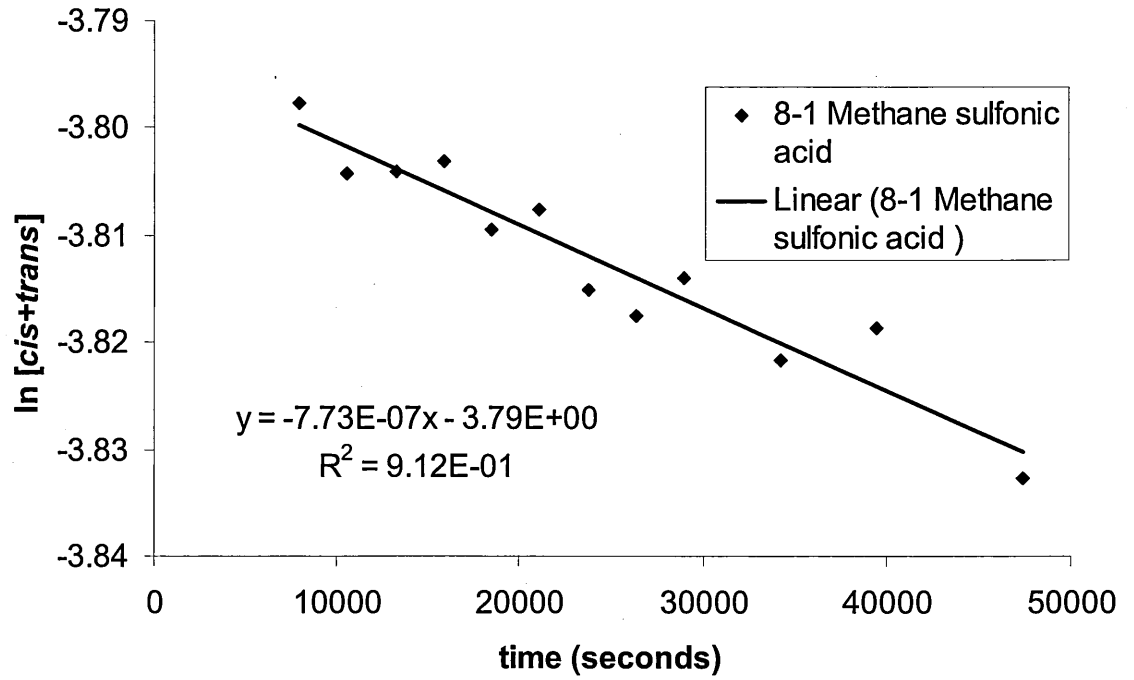


Figure B.40 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 60°C

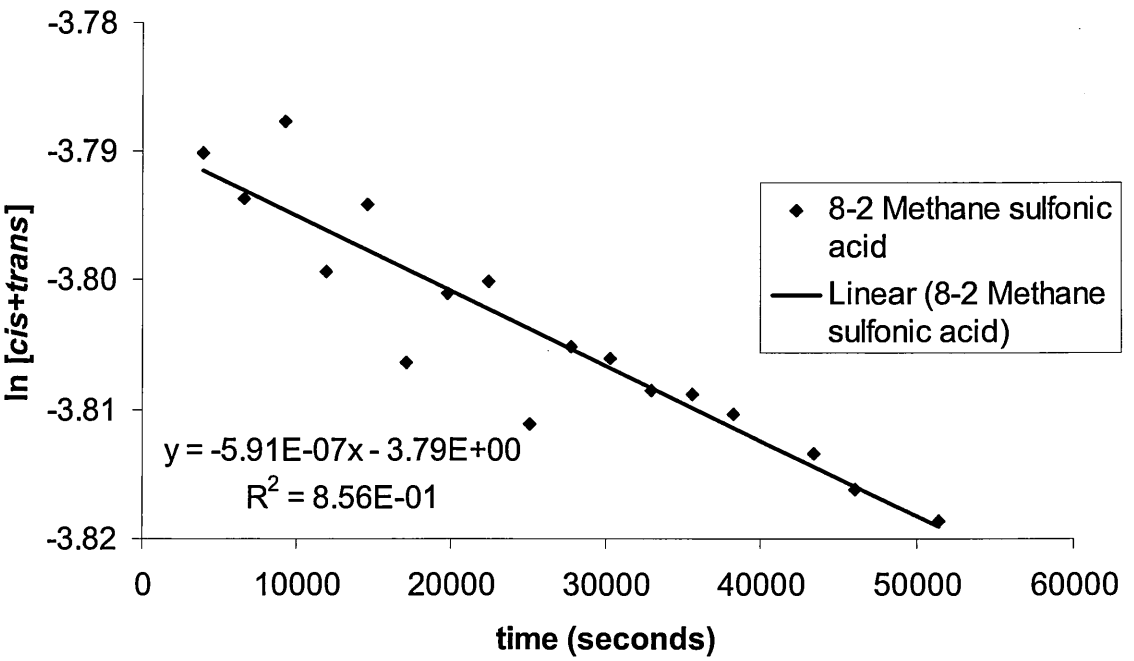


Figure B.41 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 60°C

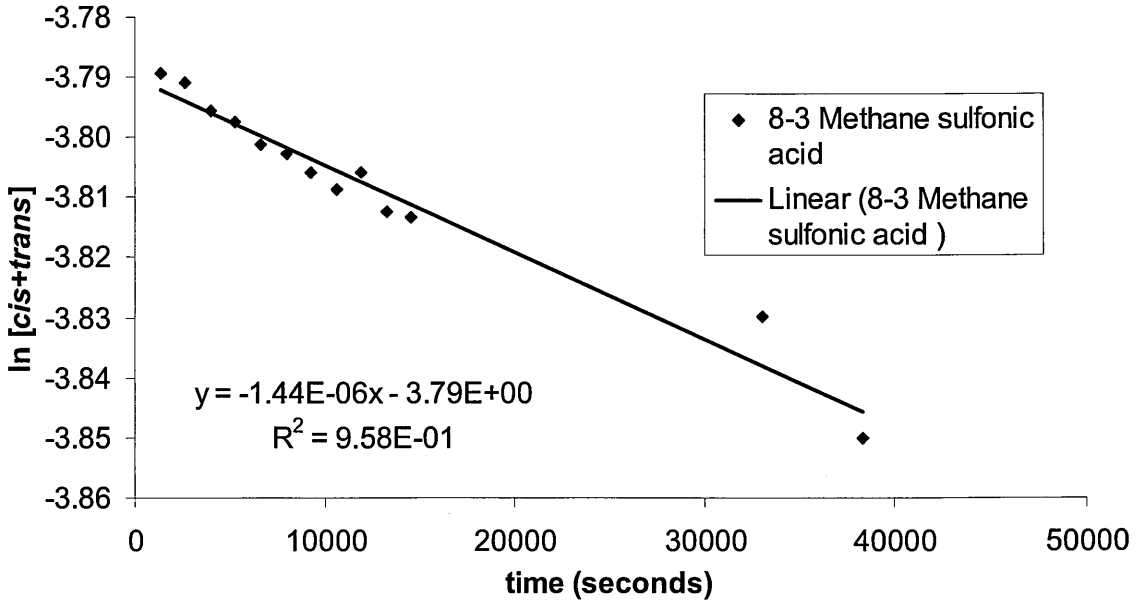


Figure B.42 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 29 mM methanesulphonic acid in nitromethane at 60°C

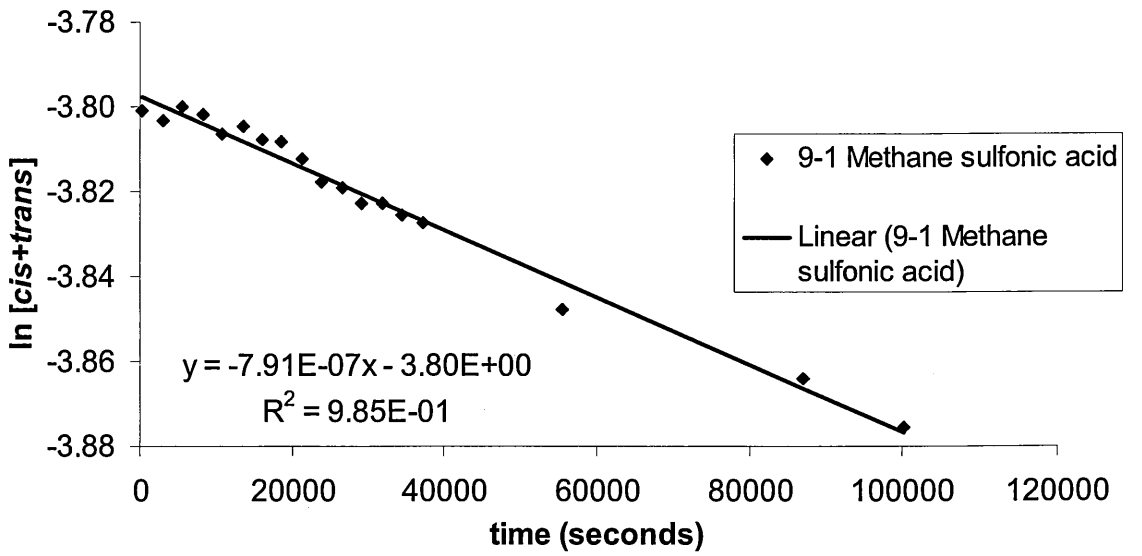


Figure B.43 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 22 mM methanesulphonic acid in nitromethane at 60°C

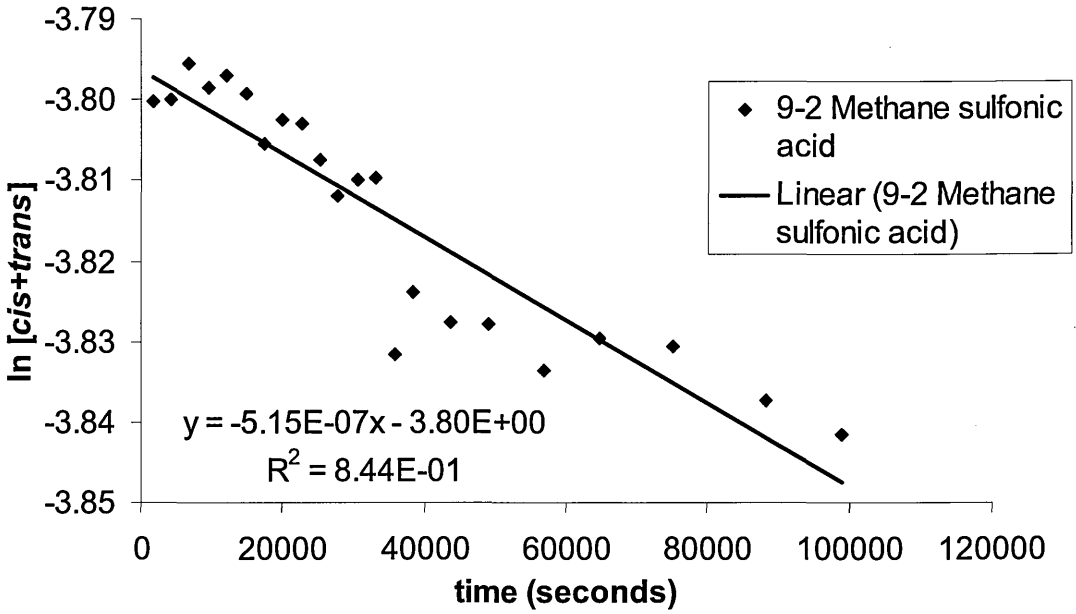


Figure B.44 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 17 mM methanesulphonic acid in nitromethane at 60°C

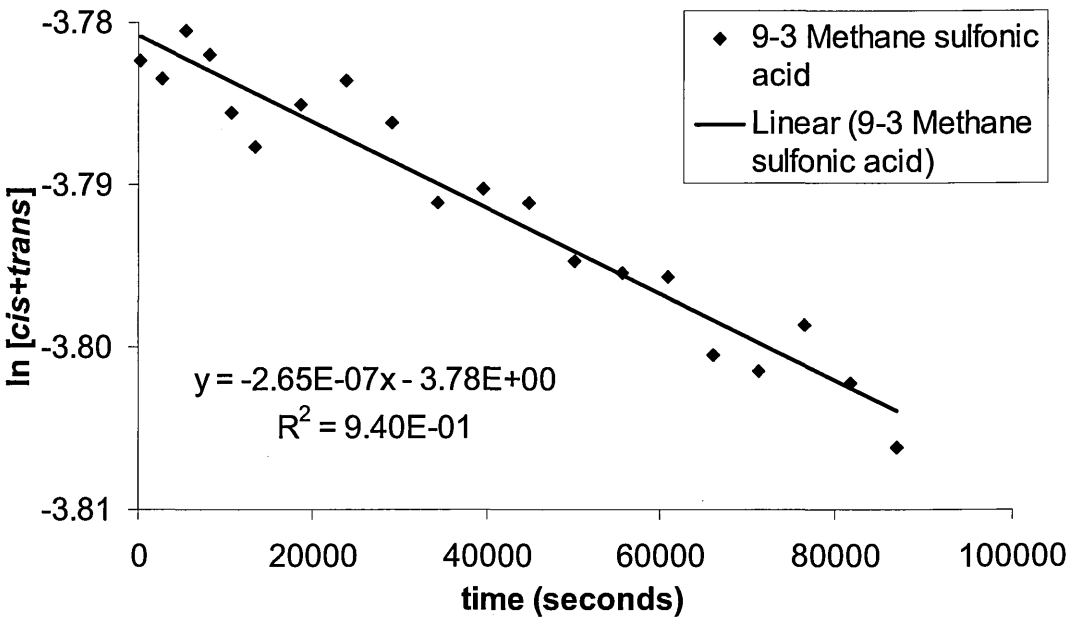


Figure B.45 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 14 mM methanesulphonic acid in nitromethane at 60°C

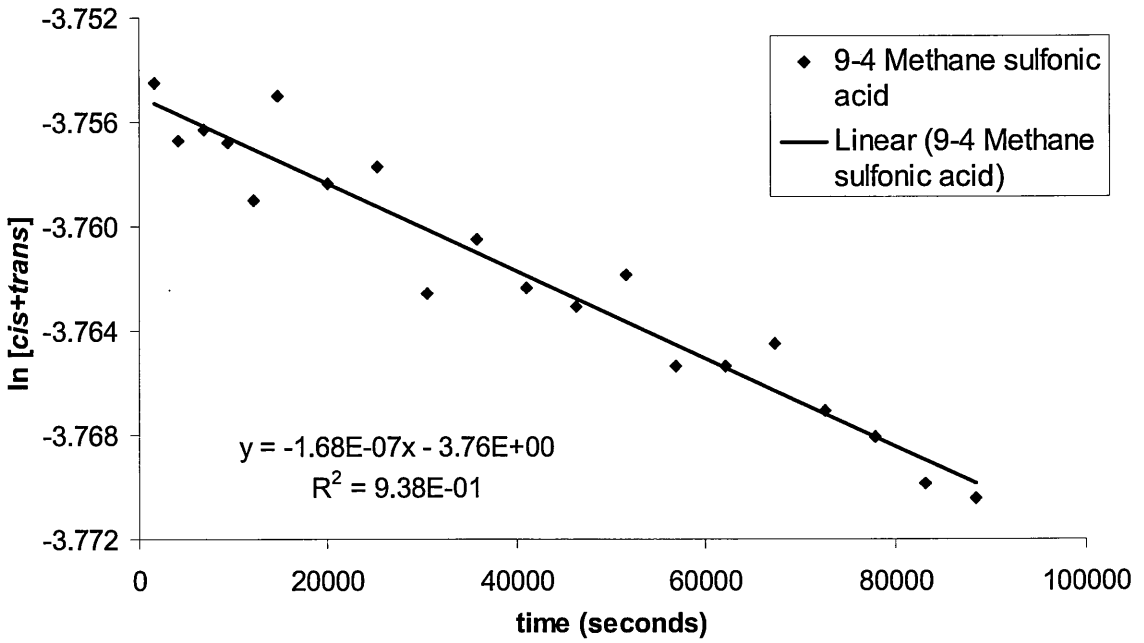


Figure B.46 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 12 mM methanesulphonic acid in nitromethane at 60°C

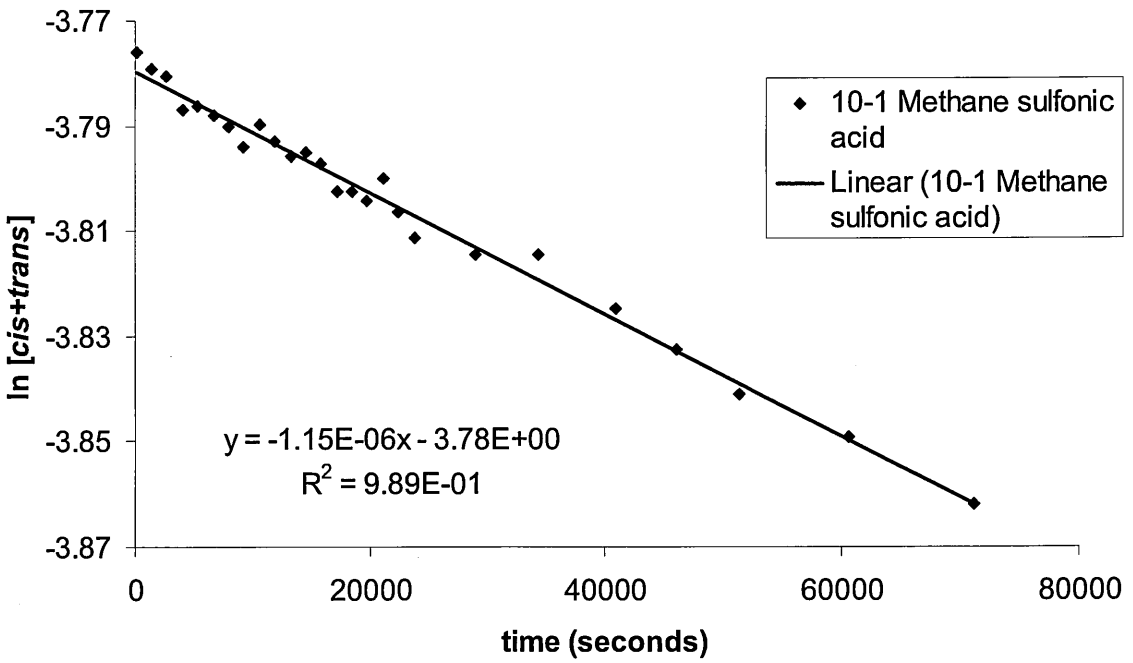


Figure B.47 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 26 mM methanesulphonic acid in nitromethane at 60°C

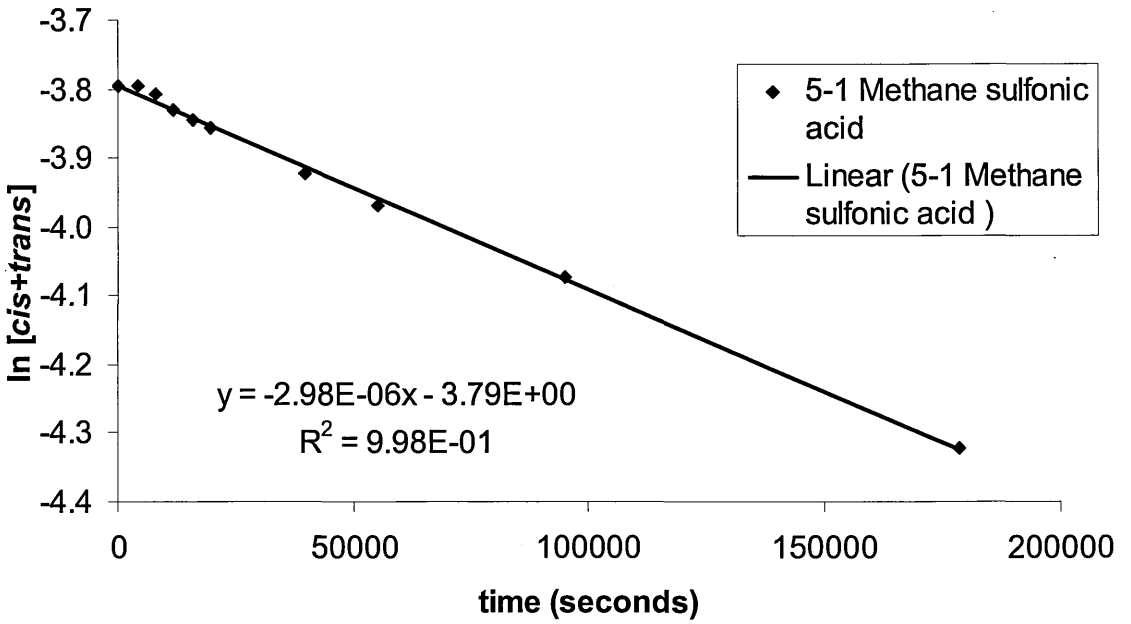


Figure B.48 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 36 mM methanesulphonic acid in nitromethane at 70°C

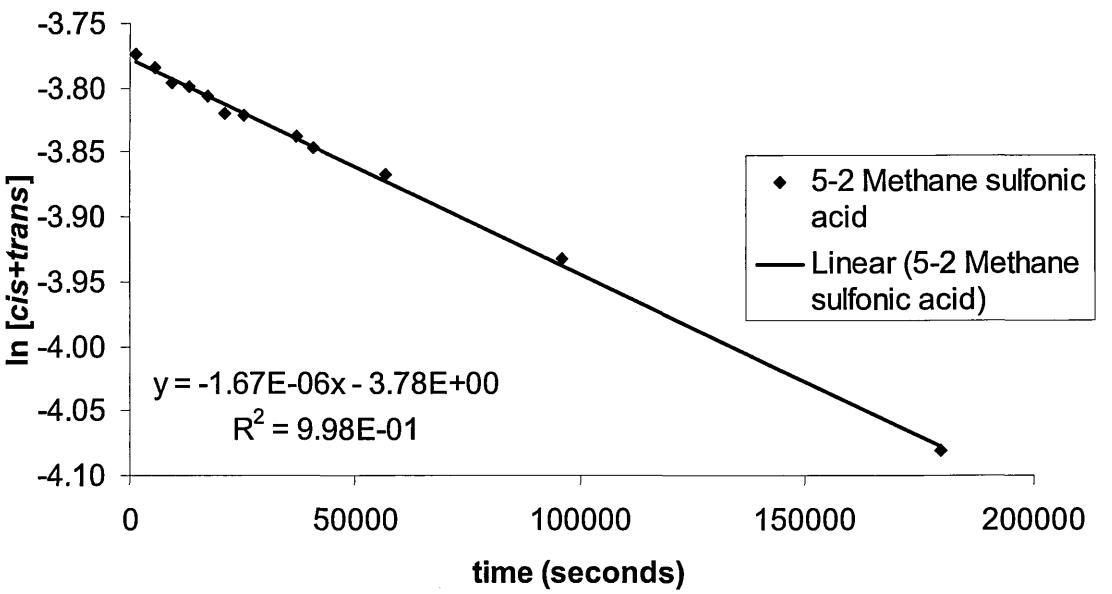


Figure B.49 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 24 mM methanesulphonic acid in nitromethane at 70°C

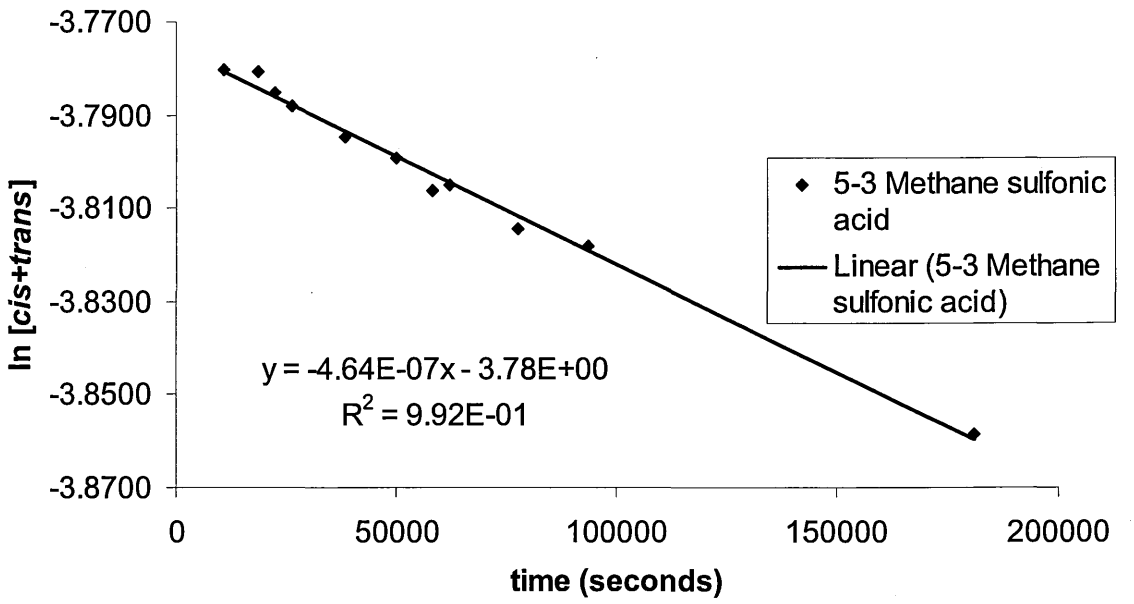


Figure B.50 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 12 mM methanesulphonic acid in nitromethane at 70°C

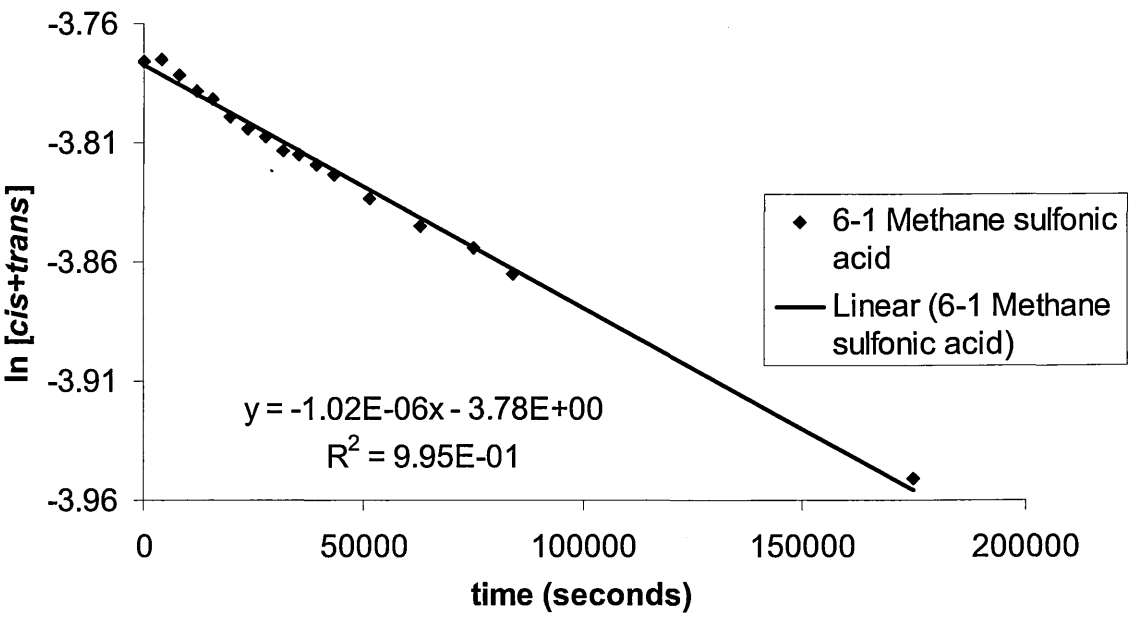


Figure B.51 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 19 mM methanesulphonic acid in nitromethane at 70°C

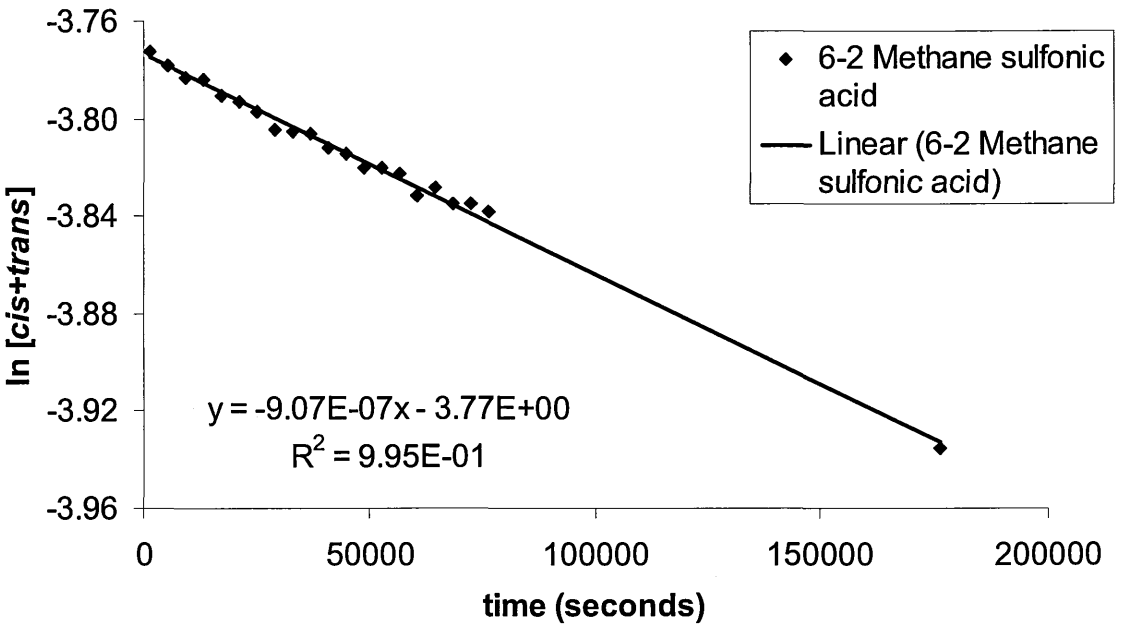


Figure B.52 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 17 mM methanesulphonic acid in nitromethane at 70°C

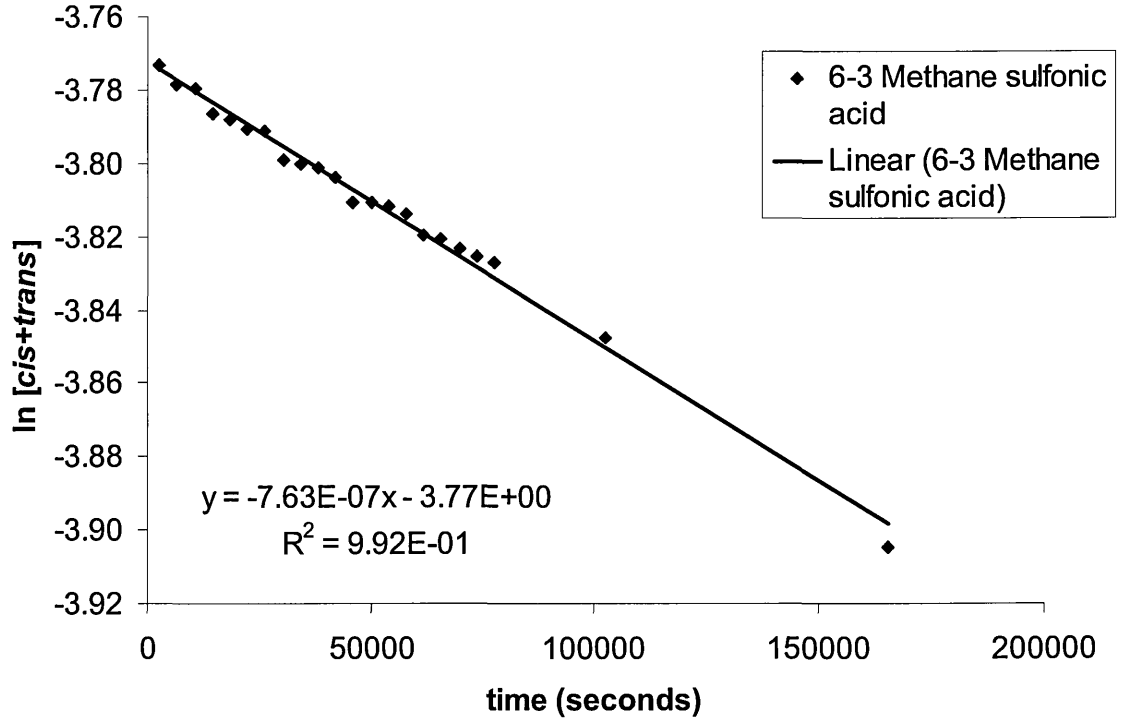


Figure B.53 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 15 mM methanesulphonic acid in nitromethane at 70°C

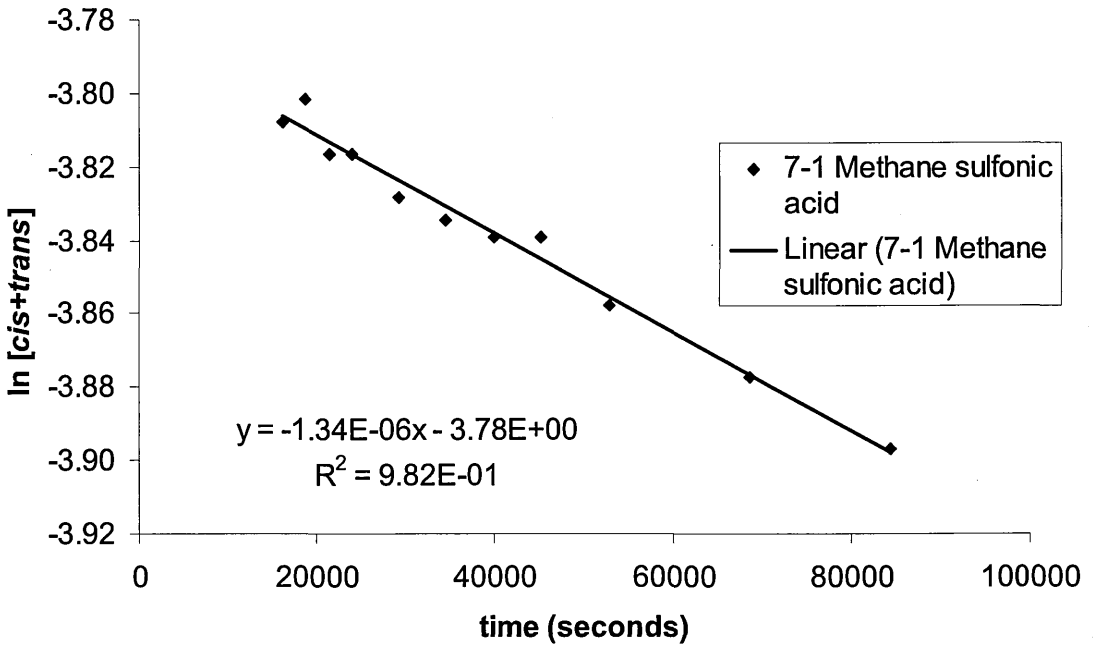


Figure B.54 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 22 mM methanesulphonic acid in nitromethane at 70°C

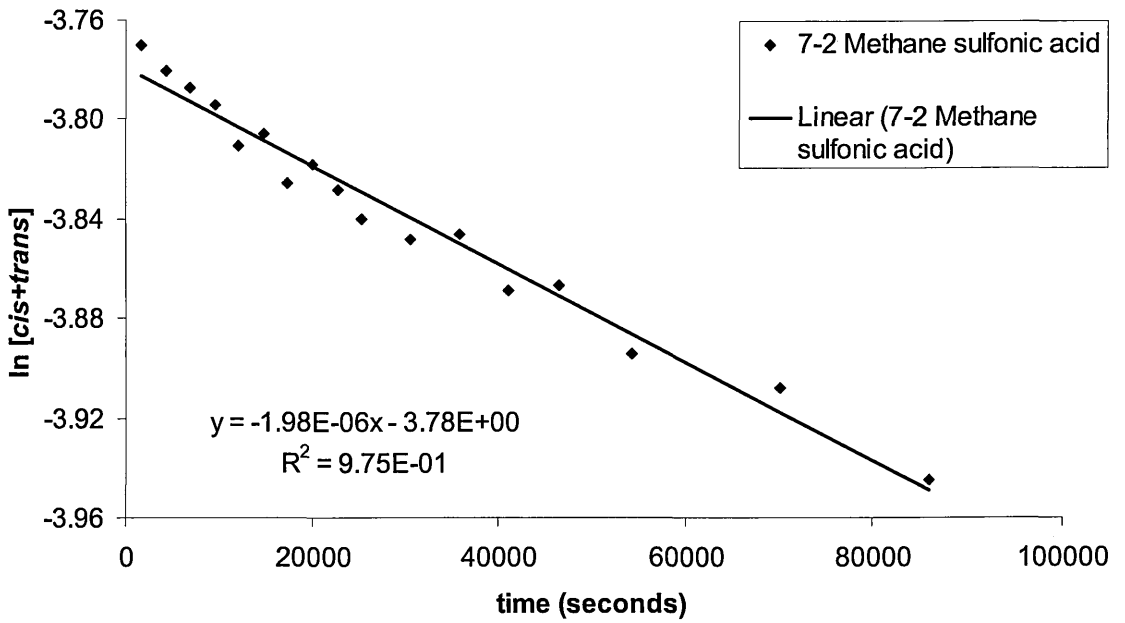


Figure B.55 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 27 mM methanesulphonic acid in nitromethane at 70°C

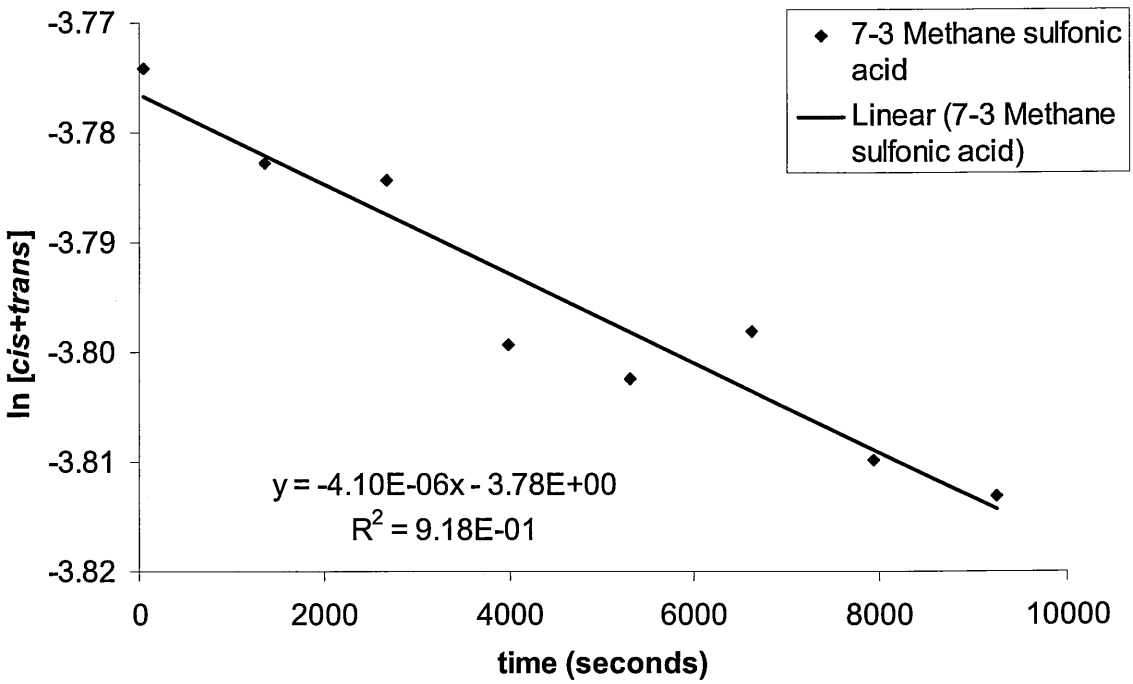


Figure B.56 Polymerisation rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 29 mM methanesulphonic acid in nitromethane at 70°C

Appendix C

Data for Interconversion Reactions Catalysed by

Iron Chloride

Appendix C. Data for Interconversion Reactions Catalysed by Iron Chloride

105-1 2,6-*cis*	time (sec)	0	46	2667	5295	7923	10549	13175	15803	18435
	% 2,6-*trans*	0	0.4	24.6	34.4	39.2	41.9	43.6	44.6	45.5
area Naphthalene	5.4min		1385.3	1434.2	1405.5	1428.1	1354.2	1370.9	1435	1373.4
area 2,6-*cis*	10.18min		877.1	651.5	530.4	510.5	460.5	459.1	478.3	448.4
area 2,6-*trans*	10.42min		3.9	212.5	277.6	329.5	332.7	354.6	385.6	373.9
Conc. 2,6-*cis*			0.0229	0.0164	0.0136	0.0129	0.0123	0.0121	0.0120	0.0118
Conc. 2,6-*trans*			0.0001	0.0053	0.0071	0.0083	0.0089	0.0093	0.0097	0.0098
[*cis*] + [*trans*]			0.0230	0.0218	0.0208	0.0212	0.0211	0.0214	0.0217	0.0216
ln [*trans* eq/*trans* eq-*trans* x]			0.0093	0.6662	1.0449	1.4160	1.6419	1.8905	2.1370	2.2404
ln [cis-*cis* eq]			-4.43	-5.22	-5.94	-6.26	-6.66	-6.82	-6.87	-7.15
1/[*cis*-*cis* eq]			88.81	208.28	493.78	765.42	1475.56	2035.53	2302.83	5319.96

105-1 2,6-*cis*			23737	29016	36949	47536	63401	84548	136118	159918
	% 2,6-*trans*		46.4	47.1	47.7	48.0	48.4	48.7	49.0	49.1
area Naphthalene			1430.8	1418.6	1392.6	1407.8	1434.1	1397	1685.2	1777.3
area 2,6-*cis*			456.7	434.5	432.5	434.7	429.6	422.8	493.6	526.7
area 2,6-*trans*			395.8	386.5	393.9	401	402.9	402.1	473.8	507.3
Conc. 2,6-*cis*			0.0115	0.0111	0.0112	0.0111	0.0108	0.0109	0.0106	0.0107
Conc. 2,6-*trans*			0.0100	0.0098	0.0102	0.0103	0.0101	0.0104	0.0102	0.0103
[*cis*] + [*trans*]			0.0215	0.0209	0.0214	0.0214	0.0210	0.0213	0.0207	0.0210
ln [*trans* eq/*trans* eq-*trans* x]			2.3857	2.2468	2.6367	2.7324	2.5528	2.8958	2.5617	2.7626
ln [cis-*cis* eq]			-7.55	-9.74	-8.45	-8.81	#NUM!	#NUM!	#NUM!	#NUM!
1/[*cis*-*cis* eq]			-13247.37	-1847.08	-2585.43	-2215.19	-1275.05	-1486.3367	-975.9306	-1110.7862

Table C.1 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.51 mM iron chloride in nitromethane at 60°C

105-2 2,6-*trans*	time (sec)	0	36	2659	5289	7916	10541	13168	15798	18452
	% 2,6-cis	0	0.9	20.4	27.9	32.5	35.5	37.6	39.3	40.7
area Naphthalene			885.5	883.8	868.6	892.4	854.9	867.0	869.0	858.5
area 2,6-*cis*			8.4	184.7	249.0	299.9	310.3	335.1	346.5	354.4
area 2,6-*trans*			941.8	720.7	642.0	623.0	564.8	555.7	535.2	517.1
Conc. 2,6-*cis*			0.0002	0.0049	0.0067	0.0078	0.0085	0.0090	0.0093	0.0096
Conc. 2,6-*trans*			0.0248	0.0190	0.0172	0.0163	0.0154	0.0149	0.0144	0.0140
ln [*cis* eq/*cis* eq-*cis* x]			0.0203	0.5851	0.9355	1.2459	1.4669	1.7106	1.8654	2.0795
ln [*trans*-*trans* eq]			-4.5284	-5.1138	-5.4648	-5.7208	-6.0307	-6.2429	-6.6005	-6.8649
[cis] + [trans]			0.0250	0.0239	0.0239	0.0241	0.0239	0.0240	0.0237	0.0237
1/[*trans*-*trans* eq]			82.7	158.4	220.6	279.6	369.8	445.6	602.5	744.2

105-2 2,6-*trans*	time (sec)	23730	29009	36943	47529	63395	84544	136116	159913
	% 2,6-cis	42.5	43.8	45.0	45.9	46.5	46.9	47.2	47.1
area Naphthalene		873.8	870.1	874.1	874.2	865.4	863.3	898.1	914.2
area 2,6-*cis*		371.5	382.7	396.9	402.7	410.0	405.7	421.2	429.5
area 2,6-*trans*		502.8	491.8	486.0	475.5	471.0	459.3	471.4	481.6
Conc. 2,6-*cis*		0.0099	0.0103	0.0106	0.0107	0.0110	0.0110	0.0109	0.0110
Conc. 2,6-*trans*		0.0134	0.0132	0.0130	0.0127	0.0127	0.0124	0.0122	0.0123
ln [*cis* eq/*cis* eq-*cis* x]		2.3143	2.6924	3.2820	3.7466	#NUM!	5.5455	5.1293	5.4766
ln [*trans*-*trans* eq]		-6.5597	-6.7434	-6.9448	-7.2904	-7.2791	-7.8125	-8.3427	-8.1710
[cis] + [trans]		0.0233	0.0234	0.0236	0.0234	0.0237	0.0234	0.0232	0.0232
1/[*trans*-*trans* eq]		1396.0	2089.4	3793.8	-55745.1	-97861.0	-3385.9	-2165.1	-2396.6

Table C.2 GC data for the interconversion reaction of 2,6-*trans*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.51 mM iron chloride in nitromethane at 60°C

94-1	time (sec)	0	49	1364	2681	4000	5318	6636	7954	9272
7.61 x10-4 mol/L FeCl3	% 2,6-*trans*	0	0.8	10.9	19.0	25.2	30.2	34.1	37.3	39.8
area Naphthalene			1455	1418.6	1407.7	1445.2	1467.3	1465.1	1442.1	1432.6
area 2,6-*cis*			873.8	743.3	668	633	614.1	576	529.9	506.5
area 2,6-*trans*			7	91.2	156.2	213.7	265.7	298.5	314.8	335.2
Conc. 2,6-*cis*	(mol/L)		0.0217	0.0189	0.0171	0.0158	0.0151	0.0142	0.0133	0.0128
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0023	0.0040	0.0053	0.0065	0.0074	0.0079	0.0084
ln [*trans* eq/*trans* eq-*trans* x]			0.0164	0.2445	0.4691	0.6911	0.9442	1.1631	1.3340	1.5584
ln [*cis-cis* eq]			-4.5023	-4.7893	-5.0309	-5.2564	-5.4013	-5.6283	-5.9268	-6.1353
cis + *trans*	(mol/L)		0.0219	0.0212	0.0211	0.0212	0.0216	0.0216	0.0211	0.0212

94-1	time (sec)	10590	11909	13227	14545	15863	17182	18500	21139
7.61 x10-4 mol/L FeCl3	% 2,6-*trans*	41.8	43.4	44.7	45.7	46.5	47.2	47.8	48.6
area Naphthalene		1447	1434.9	1433.2	1458.2	1453.6	1458	1451.1	1445.6
area 2,6-*cis*		491.6	471.7	464.2	461.4	460.3	455.1	445.6	436.9
area 2,6-*trans*		353.5	362.4	375.2	388.6	400.3	407.6	407.9	413.4
Conc. 2,6-*cis*	(mol/L)	0.0123	0.0119	0.0117	0.0114	0.0114	0.0113	0.0111	0.0109
Conc. 2,6-*trans*	(mol/L)	0.0088	0.0091	0.0095	0.0096	0.0099	0.0101	0.0101	0.0103
ln [*trans* eq/*trans* eq-*trans* x]		1.7392	1.9121	2.1488	2.2949	2.6484	2.8705	2.9664	3.3512
ln [*cis-cis* eq]		-6.3971	-6.6695	-6.8178	-7.1009	-7.0903	-7.3084	-7.6270	-8.0725
cis + *trans*	(mol/L)	0.0211	0.0210	0.0211	0.0210	0.0214	0.0214	0.0212	0.0212

Table C.3 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM iron chloride in nitromethane at 40°C

94-2	time (sec)	0	54	1376	2698	4022	5344	6668	7991
5.07 x10-4 mol/L FeCl3	% 2,6-*trans*	0	0.5	4.7	8.5	11.9	15.0	17.7	20.2
area Naphthalene	7.9		1466.6	1462.8	1481.4	1435.5	1447.4	1449.7	1456.4
area 2,6-*cis*	10.18		873.8	845.5	812.4	764.2	722.1	719.6	693.9
area 2,6-*trans*	10.42		4.1	41.5	75.5	103.5	127.6	155.2	176.0
Conc. 2,6-*cis*			0.0215	0.0209	0.0198	0.0192	0.0180	0.0179	0.0172
Conc. 2,6-*trans*			0.0001	0.0010	0.0018	0.0026	0.0032	0.0039	0.0044
ln [*trans* eq/*trans* eq-*trans* x]			0.0094	0.1001	0.1877	0.2773	0.3511	0.4456	0.5207
ln [*cis*-*cis* eq]			-4.5271	-4.5884	-4.6995	-4.7652	-4.9181	-4.9306	-5.0356
cis + *trans*	(mol/L)		0.0216	0.0219	0.0216	0.0218	0.0212	0.0218	0.0216

94-2	time (sec)	9315	10639	11961	13283	14606	15929	17356
5.07 x10-4 mol/L FeCl3	% 2,6-*trans*	22.5	24.5	26.4	28.1	29.6	31.0	32.4
area Naphthalene	7.9	1484.5	1497.8	1421.1	1410.4	1427.7	1421.4	1411.4
area 2,6-*cis*	10.18	687.5	678.4	629.7	607.6	604.6	575.2	569.0
area 2,6-*trans*	10.42	199.3	220.4	225.8	237.0	254.3	258.8	272.1
Conc. 2,6-*cis*		0.0167	0.0164	0.0160	0.0156	0.0153	0.0146	0.0146
Conc. 2,6-*trans*		0.0048	0.0053	0.0057	0.0061	0.0064	0.0066	0.0070
ln [*trans* eq/*trans* eq-*trans* x]		0.5995	0.6817	0.7628	0.8310	0.9119	0.9455	1.0427
ln [*cis*-*cis* eq]		-5.1125	-5.1755	-5.2403	-5.3279	-5.3839	-5.5440	-5.5582
cis + *trans*	(mol/L)	0.0216	0.0217	0.0217	0.0216	0.0217	0.0212	0.0215

Table C.4 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.51 mM iron chloride in nitromethane at 40°C

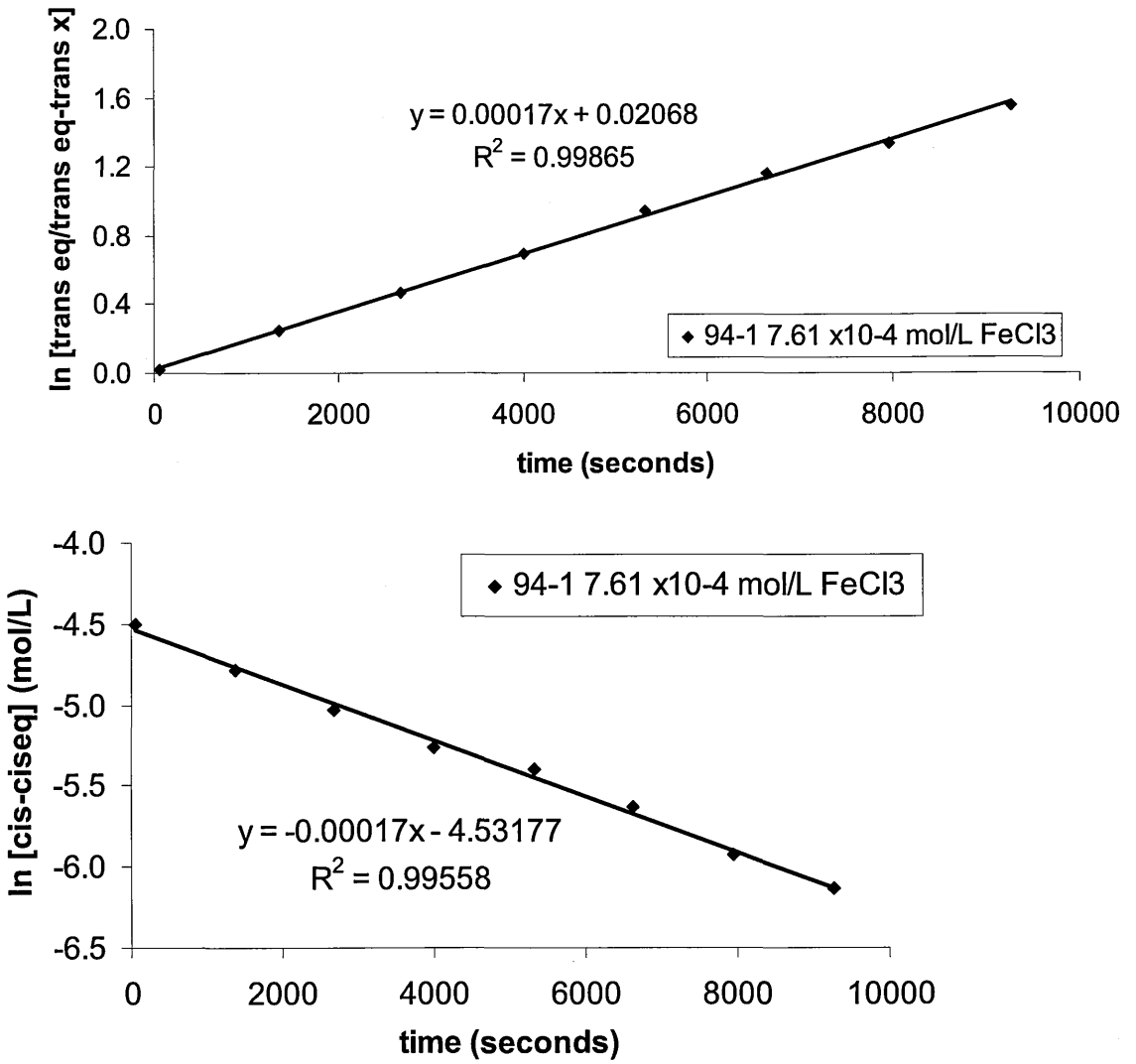


Figure C.1 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM iron chloride in nitromethane at 40°C

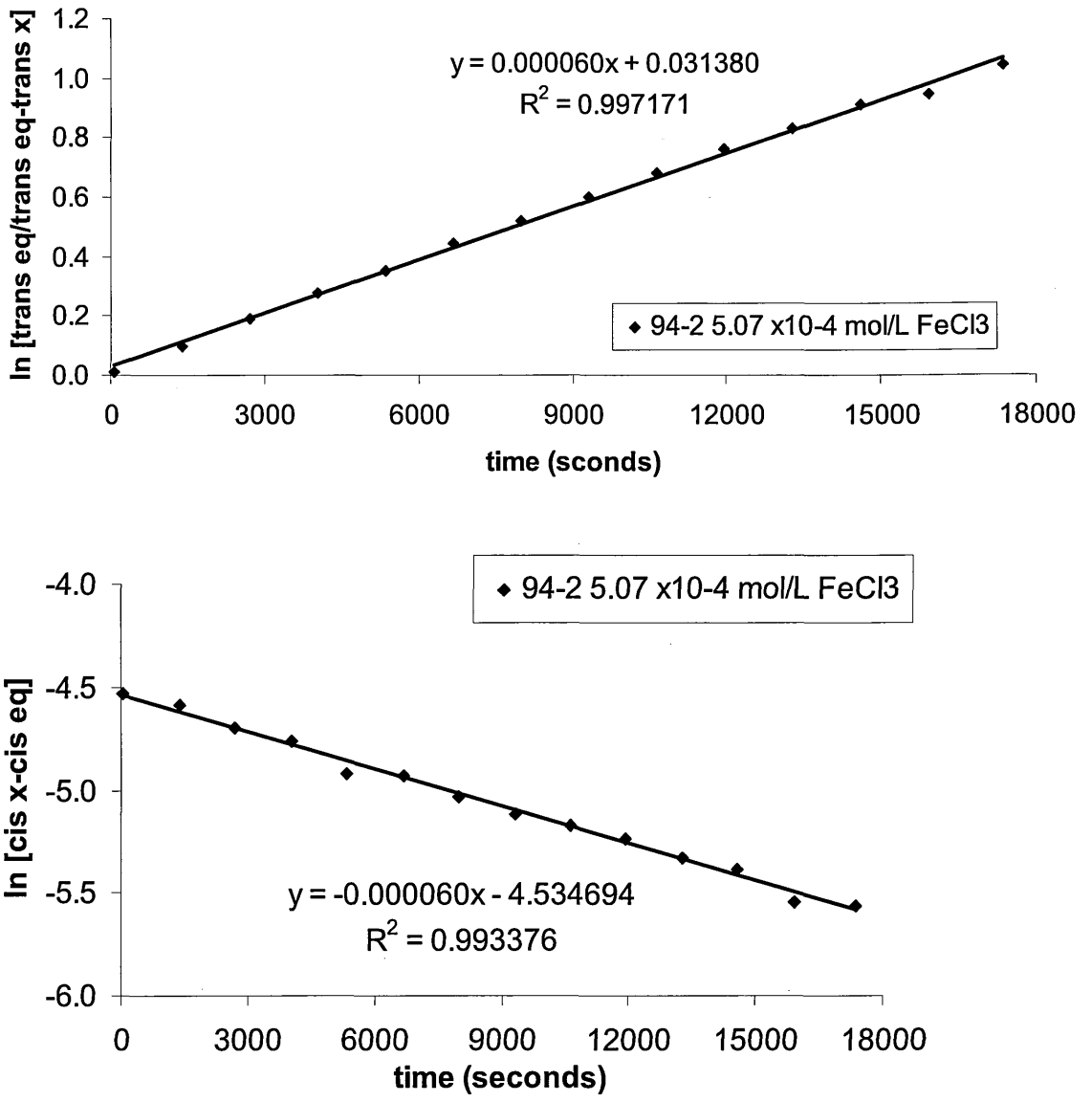


Figure C.2 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.51 mM iron chloride in nitromethane at 40°C

92-1, 92-2	time (sec)	0	40	1354	2671	3988	617
7.61 x10-4 mol/L FeCl3	% 2,6-*trans*	0	1.3	20.6	32.3	39.2	9.7
area Naphthalene			1570.5	1513	1467.2	1491.7	1489.6
area 2,6-*cis*			913.5	689.7	595.2	517.6	794.9
area 2,6-*trans*			12	178.7	284.1	334.3	85.5
Conc. 2,6-*cis*	(mol/L)		0.0210	0.0165	0.0146	0.0125	0.0193
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0043	0.0070	0.0081	0.0021
ln [*trans* eq/*trans* eq-*trans* x]			0.0266	0.5211	1.0961	1.4723	0.2199
ln [*cis-cis* eq]			-4.5468	-5.1063	-5.4616	-6.1526	-4.7254
cis + *trans*	(mol/L)		0.0213	0.0207	0.0216	0.0206	0.0213

92-1, 92-2	time (sec)	1930	3244	9260	10459
7.61 x10-4 mol/L FeCl3	% 2,6-*trans*	26.1	35.6	48.5	49.1
area Naphthalene		1511.4	1459.8	1532.6	1600.8
area 2,6-*cis*		645.0	557.5	444.7	463.7
area 2,6-*trans*		227.6	307.8	418.8	447.5
Conc. 2,6-*cis*	(mol/L)	0.0154	0.0138	0.0105	0.0105
Conc. 2,6-*trans*	(mol/L)	0.0054	0.0076	0.0099	0.0101
ln [*trans* eq/*trans* eq-*trans* x]		0.7294	1.2911	2.8073	3.2507
ln [*cis-cis* eq]		-5.2967	-5.6873	-9.4806	-9.7460
cis + *trans*	(mol/L)	0.0208	0.0214	0.0203	0.0206

Table C.5 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM iron chloride in nitromethane at 50°C

93-1	time (sec)	0	38	1375	2692	4009	5339	6656	7973	9306	10624
5.07 x10-4 mol/L FeCl3	% 2,6-*trans*	0	0.5	9.6	16.7	22.4	26.9	30.7	33.7	36.2	38.4
area Naphthalene	7.9		1449.1	1487.9	1553.1	1428.0	1448.5	1476.2	1479.9	1466.9	1499.7
area 2,6-*cis*	10.18		846.9	791.9	741.9	639.7	628.1	605.8	590.1	548.1	556.6
area 2,6-*trans*	10.42		4.1	83.9	149.2	184.5	231.3	268.4	300.5	311.3	346.8
Conc. 2,6-*cis*			0.0211	0.0192	0.0172	0.0162	0.0157	0.0148	0.0144	0.0135	0.0134
Conc. 2,6-*trans*			0.0001	0.0020	0.0035	0.0047	0.0058	0.0066	0.0073	0.0077	0.0083
ln [*trans* eq/*trans* eq-*trans* x]			0.0092	0.2026	0.3747	0.5452	0.7327	0.8950	1.0802	1.1721	1.3951
ln [*cis*-*cis* eq]			-4.5853	-4.7896	-5.0598	-5.2450	-5.3483	-5.5425	-5.6559	-5.9559	-5.9914
cis + *trans*	(mol/L)		0.0212	0.0213	0.0207	0.0208	0.0214	0.0214	0.0217	0.0212	0.0217

93-1	time (sec)	15907	17236	18552	19860	21199	22517	23834	25165	26480
5.07 x10-4 mol/L FeCl3	% 2,6-*trans*	43.7	44.5	45.2	45.9	46.3	46.8	47.2	47.5	47.9
area Naphthalene	7.9	1494.1	1494.9	1494.3	1428.4	1481.4	1506.6	1486.9	1476.5	1497.0
area 2,6-*cis*	10.18	505.8	499.4	478.6	451.2	468.7	483.8	473.4	461.7	470.2
area 2,6-*trans*	10.42	392.4	399.8	395.4	382.2	404.4	426.1	423.6	417.5	431.5
Conc. 2,6-*cis*		0.0122	0.0121	0.0116	0.0114	0.0114	0.0116	0.0115	0.0113	0.0113
Conc. 2,6-*trans*		0.0095	0.0097	0.0096	0.0097	0.0099	0.0102	0.0103	0.0102	0.0104
ln [*trans* eq/*trans* eq-*trans* x]		1.9260	2.0396	1.9710	2.0428	2.1888	2.5250	2.6127	2.5226	2.7738
ln [*cis*-*cis* eq]		-6.6280	-6.7579	-7.3173	-7.5912	-7.5553	-7.2728	-7.4266	-7.8492	-7.7277
cis + *trans*	(mol/L)	0.0217	0.0217	0.0211	0.0211	0.0213	0.0218	0.0218	0.0215	0.0217

Table C.6 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.51 mM iron chloride in nitromethane at 50°C

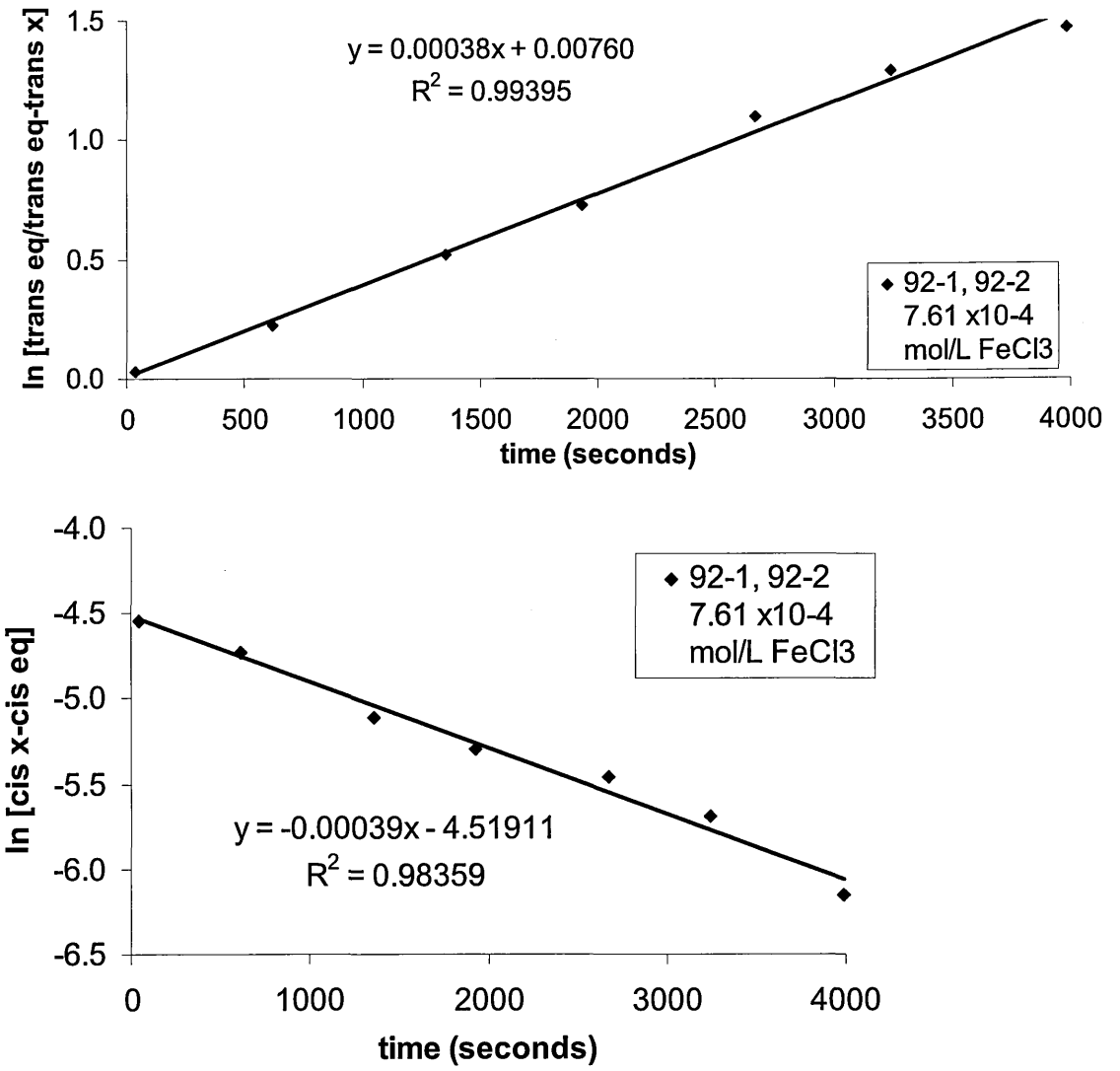


Figure C.3 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM iron chloride in nitromethane at 50°C

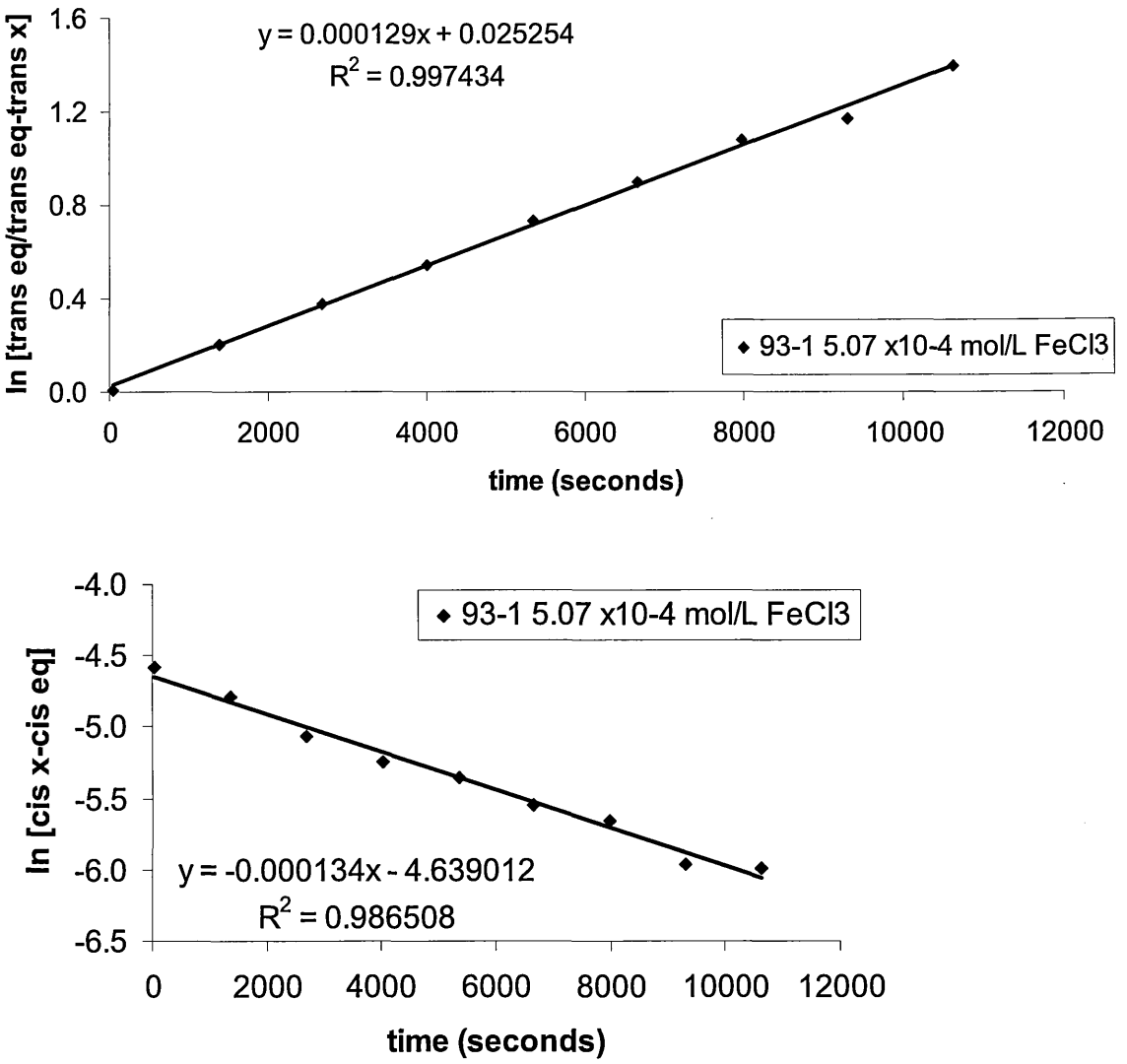


Figure C.4 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.51 mM iron chloride in nitromethane at 50°C

90-1, 90-2, 90-3, 90-4	time (sec)	0	42	1358	364	1679
7.61 x10-4 mol/L FeCl3	% 2,6-*trans*	0	1.5	34.1	8.4	33.4
area Naphthalene			1528	1477	1463.5	1473.6
area 2,6-*cis*			857.6	581.6	795.3	575.3
area 2,6-*trans*			13.2	300.3	72.6	288.0
Conc. 2,6-*cis*	(mol/L)		0.0203	0.0142	0.0196	0.0141
Conc. 2,6-*trans*	(mol/L)		0.0003	0.0073	0.0018	0.0071
ln [*trans* eq/*trans* eq-*trans* x]			0.0302	1.2011	0.1870	1.1149
ln [*cis*-*cis* eq]			-4.6188	-5.5682	-4.6863	-5.6006
cis + *trans*	(mol/L)		0.0206	0.0216	0.0214	0.0212

90-1, 90-2, 90-3, 90-4	time (sec)	631	1945	923	2236
7.61 x10-4 mol/L FeCl3	% 2,6-*trans*	14.2	33.6	23.3	40.0
area Naphthalene		1570.1	1569.8	1511.0	1479.9
area 2,6-*cis*		770.7	588.8	703.5	525.5
area 2,6-*trans*		127.5	297.5	213.6	350.4
Conc. 2,6-*cis*	(mol/L)	0.0177	0.0135	0.0168	0.0128
Conc. 2,6-*trans*	(mol/L)	0.0029	0.0068	0.0051	0.0085
ln [*trans* eq/*trans* eq-*trans* x]		0.3274	1.0546	0.6657	1.6829
ln [*cis*-*cis* eq]		-4.9168	-5.7628	-5.0499	-6.0237
cis + *trans*	(mol/L)	0.0207	0.0204	0.0219	0.0214

Table C.7 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM iron chloride in nitromethane at 60°C

91-1, 91-2	time (sec)	0	632	1945	57	1369
5.07 x10-4 mol/L FeCl3	% 2,6-*trans*	0	8.7	23.3	0.7	30.2
area Naphthalene			1521.2	1460	1409.2	1437.0
area 2,6-*cis*			852.9	668.9	836.0	552.7
area 2,6-*trans*			81.2	202.8	5.8	239.7
Conc. 2,6-*cis*	(mol/L)		0.0199	0.0163	0.0211	0.0137
Conc. 2,6-*trans*	(mol/L)		0.0019	0.0050	0.0001	0.0060
ln [*trans* eq/*trans* eq-*trans* x]			0.2028	0.6494	0.0143	0.8523
ln [*cis-cis* eq]			-4.6619	-5.1498	-4.5462	-5.7495
cis + *trans*	(mol/L)		0.0219	0.0213	0.0213	0.0197

91-1, 91-2	time (sec)	3261	4603	8570	9886
5.07 x10-4 mol/L FeCl3	% 2,6-*trans*	32.2	37.8	45.7	46.9
area Naphthalene		1507.5	1466.7	1527.2	1512.4
area 2,6-*cis*		614.1	530.7	475.8	462.7
area 2,6-*trans*		291.2	323.1	399.7	408.6
Conc. 2,6-*cis*	(mol/L)	0.0145	0.0129	0.0111	0.0109
Conc. 2,6-*trans*	(mol/L)	0.0070	0.0080	0.0094	0.0098
ln [*trans* eq/*trans* eq-*trans* x]		1.0913	1.4167	2.3021	2.6450
ln [*cis-cis* eq]		-5.5231	-6.0433	-7.4445	-7.8624
cis + *trans*	(mol/L)	0.0215	0.0208	0.0205	0.0206

Table C.8 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.51 mM iron chloride in nitromethane at 60°C

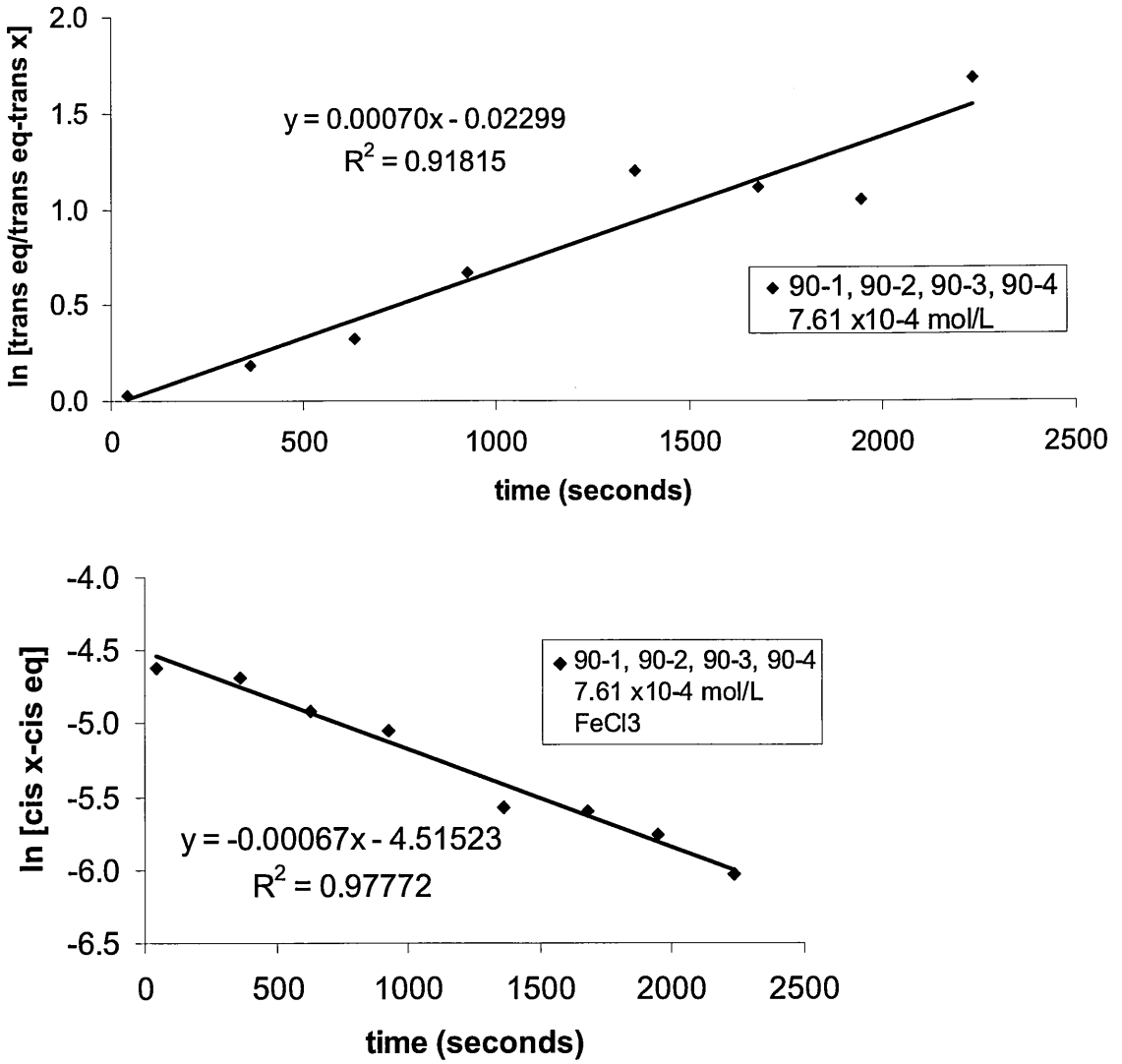


Figure C.5 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM iron chloride in nitromethane at 60°C

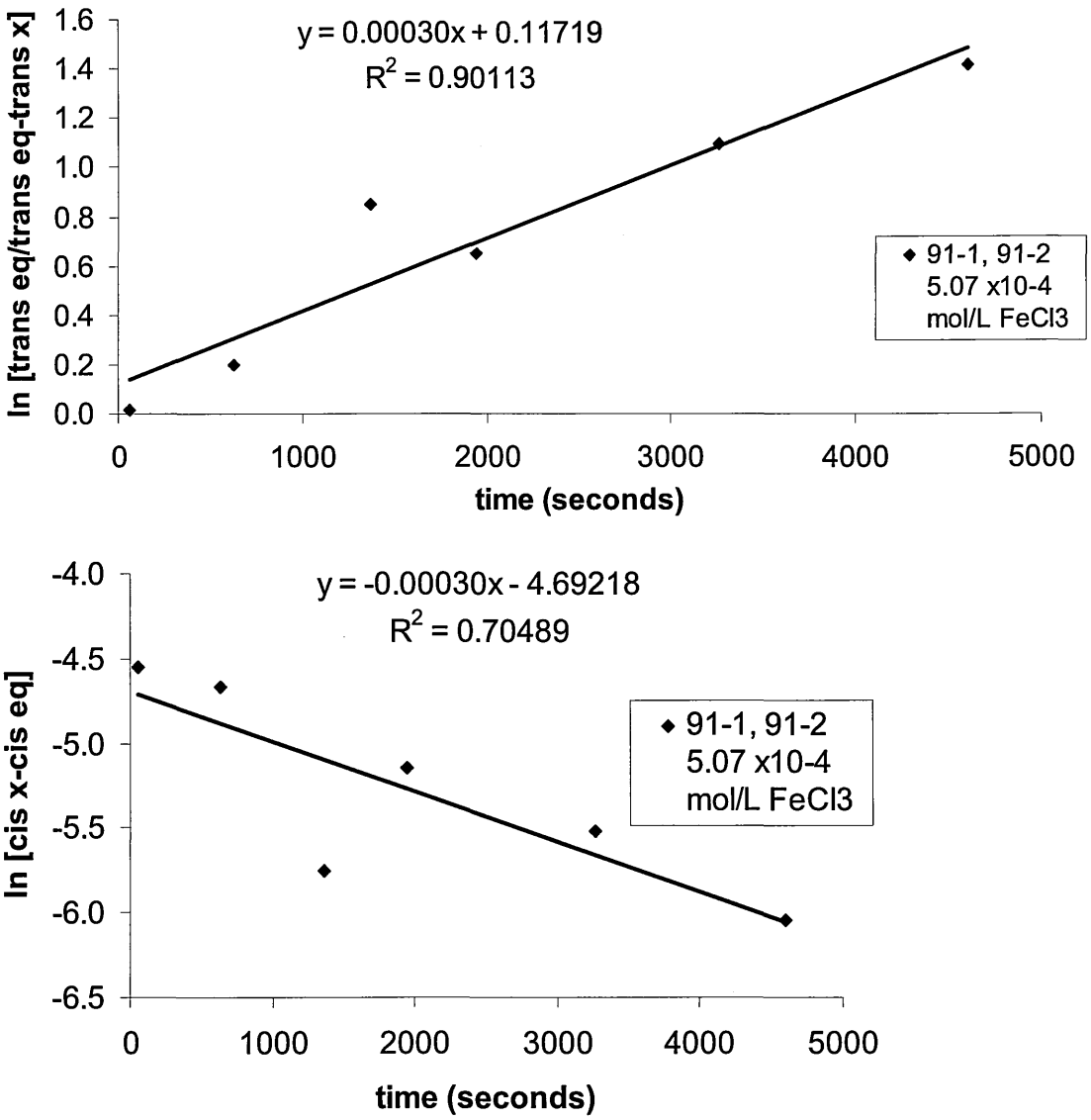


Figure C.6 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.51 mM iron chloride in nitromethane at 60°C

88-1, 88-2, 88-3, 88-4	time (sec)	0	47	370	667	935	5321
7.61 x10-4 mol/L FeCl3	% 2,6-*trans*	0	0.00001	14.9	22.6	30.6	49.9
area Naphthalene			1399	1490	1477.8	1498.8	1472.4
area 2,6-*cis*			830.6	708.9	655.6	578.3	410.5
area 2,6-*trans*			7	123.7	191.0	255.2	409.5
Conc. 2,6-*cis*	(mol/L)		0.0214	0.0172	0.0160	0.0139	0.0101
Conc. 2,6-*trans*	(mol/L)		0.0002	0.0030	0.0047	0.0061	0.0100
ln [*trans* eq/*trans* eq-*trans* x]			0.0182	0.3563	0.6286	0.9539	#NUM!
ln [*cis*-*cis* eq]			-4.4536	-4.9093	-5.0804	-5.4893	-8.2319
cis + *trans*	(mol/L)		0.0216	0.0202	0.0207	0.0201	0.0201

88-1, 88-2, 88-3, 88-4	time (sec)		6642	7963	9284	19854	30421
7.61 x10-4 mol/L FeCl3	% 2,6-*trans*		50.1	50.2	50.2	50.3	50.2
area Naphthalene			1484.3	1501.4	1444.7	1517	1475.7
area 2,6-*cis*			413.9	420	402.5	418.3	396.1
area 2,6-*trans*			415.7	423.2	406.4	422.8	400
Conc. 2,6-*cis*	(mol/L)		0.0101	0.0101	0.0101	0.0100	0.0097
Conc. 2,6-*trans*	(mol/L)		0.0101	0.0102	0.0102	0.0101	0.0098
ln [*trans* eq/*trans* eq-*trans* x]		#NUM!		#NUM!	#NUM!	#NUM!	3.8472
ln [*cis*-*cis* eq]			-8.2244	-8.1116	-8.2583	-8.7674	#NUM!
cis + *trans*	(mol/L)		0.0202	0.0203	0.0202	0.0200	0.0195

Table C.9 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM iron chloride in nitromethane at 70°C

89-1, 89-2, 89-3, 89-4	time (sec)	0	329	1643	632	1946	160
5.07 x10-4 mol/L FeCl3	% 2,6-*trans*	0	6.0	28.2	12.7	30.3	0.466
area Naphthalene			1533.7	1505.4	1505.3	1526.7	1533.7
area 2,6-*cis*			868.8	623.6	752.3	601.7	853.8
area 2,6-*trans*			55.9	244.6	109.9	261.8	4
Conc. 2,6-*cis*	(mol/L)		0.02045	0.01496	0.01804	0.01423	0.02010
Conc. 2,6-*trans*	(mol/L)		0.00132	0.00587	0.00264	0.00619	0.00009
ln [*trans* eq/*trans* eq-*trans* x]			0.1396	0.8695	0.3024	0.9493	0.0094
ln [*cis-cis* eq]			-4.5609	-5.3071	-4.8228	-5.4656	-4.5953
cis + *trans*	(mol/L)		0.0218	0.0208	0.0207	0.0204	0.0202

89-1, 89-2, 89-3, 89-4	time (sec)	1476	926	2238	10882	19232
5.07 x10-4 mol/L FeCl3	% 2,6-*trans*	25.9	18.0	33.6	49.0	49.8
area Naphthalene		1494.2	1535.5	1530	1462	1506
area 2,6-*cis*		621	722.6	566.6	426.2	417.8
area 2,6-*trans*		217.6	158.8	286.8	409.7	413.8
Conc. 2,6-*cis*	(mol/L)	0.01501	0.01699	0.01337	0.01053	0.01002
Conc. 2,6-*trans*	(mol/L)	0.00526	0.00373	0.00677	0.01012	0.00992
ln [*trans* eq/*trans* eq-*trans* x]		0.7352	0.4616	1.1090	#NUM!	4.0304
ln [*cis-cis* eq]		-5.2972	-4.9631	-5.6926	-7.5514	-11.0150
cis + *trans*	(mol/L)	0.0203	0.0207	0.0201	0.0206	0.0199

Table C.10 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.51 mM iron chloride in nitromethane at 70°C

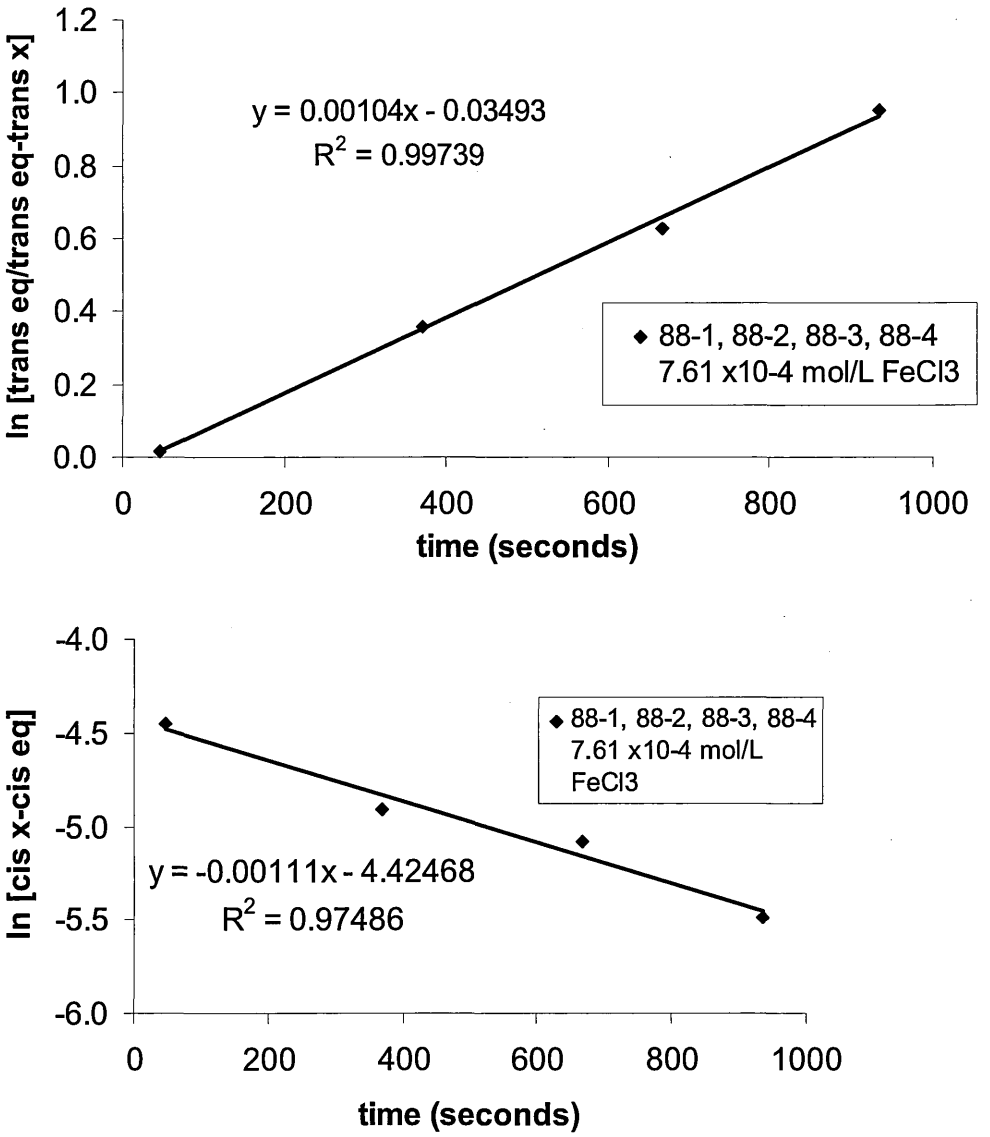
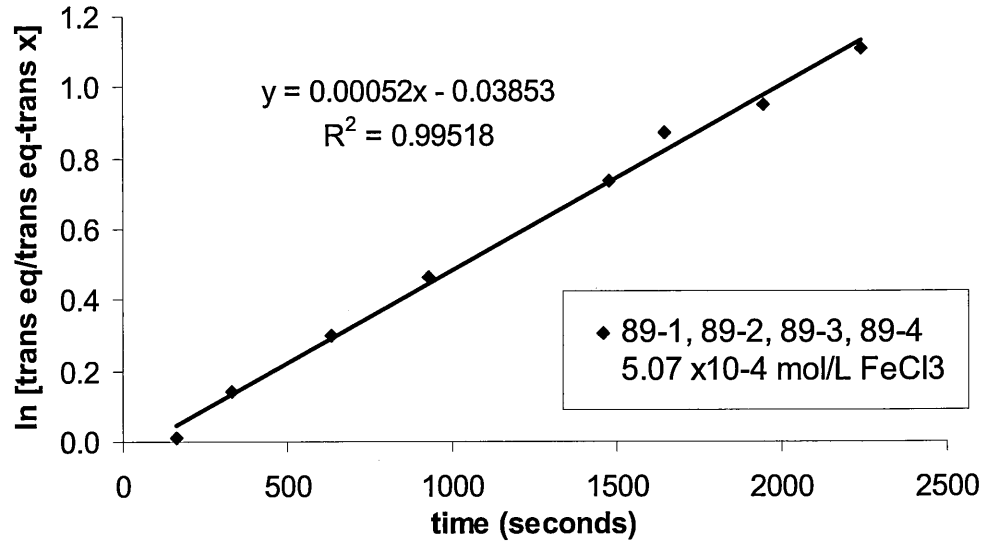


Figure C.7 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.76 mM iron chloride in nitromethane at 70°C



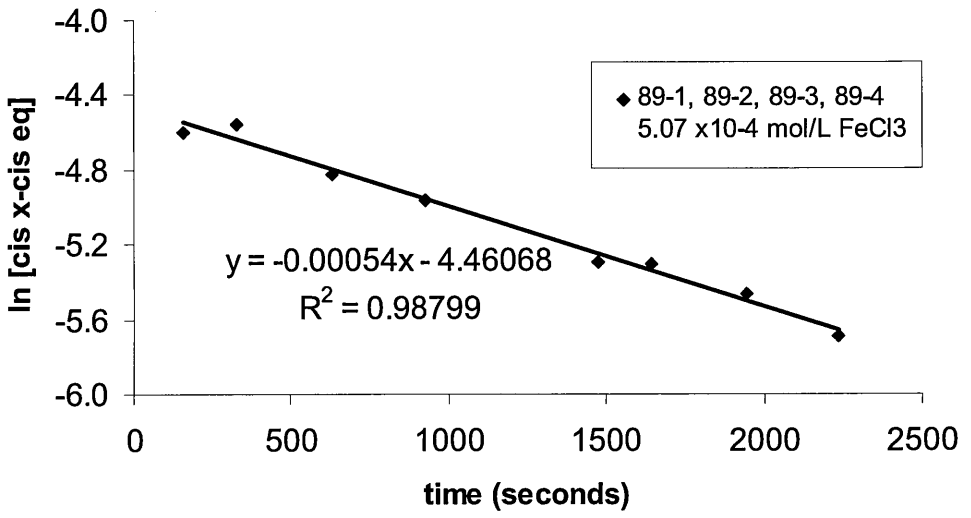


Figure C.8 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.51 mM iron chloride in nitromethane at 70°C

122-1 (50ppm water)	time (sec)	0	85	4020	7977	11924	15870	19816	23761
	% 2,6-*trans*	0	0.6	44.6	49.3	50.1	50.2	50.3	50.3
area Naphthalene	5.4		304.7	302.5	301.6	305.1	302.9	303.9	304.4
area 2,6-*cis*	10.18		582.4	320.1	291.9	288.9	286.1	285.9	285.9
area 2,6-*trans*	10.42		3.7	257.2	284	289.7	288.4	288.9	289.1
Conc. 2,6-*cis*	(mol/L)		0.0690	0.0382	0.0349	0.0342	0.0341	0.0340	0.0339
Conc. 2,6-*trans*	(mol/L)		0.0004	0.0307	0.0340	0.0343	0.0344	0.0343	0.0343
ln [*trans* eq/*trans* eq-*trans* x]			0.0126	2.0964	3.5537	3.8878	4.0284	3.9457	3.8986
ln [*cis-cis* eq]			-3.3811	-5.7428	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
cis + *trans*	(mol/L)		0.0694	0.0689	0.0689	0.0685	0.0685	0.0683	0.0682
	59.9C	11/7/02 7:31am							
122-2 (140ppm water)	time (sec)	0	1399	5347	9293	13239	17185	21130	25077
	% 2,6-*trans*	0	12.4	30.9	38.6	42.4	44.5	45.8	46.5
area Naphthalene	5.4		305.2	305.6	307.3	306.9	303.6	307.7	307.7
area 2,6-*cis*	10.18		515.2	405.5	362	338.4	322.8	320.5	313.2
area 2,6-*trans*	10.42		72.8	181.7	227.3	249.2	258.3	270.5	272.7
Conc. 2,6-*cis*	(mol/L)		0.0609	0.0479	0.0425	0.0398	0.0384	0.0376	0.0368
Conc. 2,6-*trans*	(mol/L)		0.0086	0.0215	0.0267	0.0293	0.0307	0.0317	0.0320
ln [*trans* eq/*trans* eq-*trans* x]			0.2824	0.9502	1.4398	1.8179	2.1009	2.3737	2.4562
ln [*cis-cis* eq]			-3.6516	-4.3499	-4.8886	-5.3368	-5.6873	-5.9495	-6.3478
cis + *trans*	(mol/L)		0.0696	0.0694	0.0692	0.0691	0.0691	0.0693	0.0687
	59.9C	11/7/02 7:31am							
122-3 (220ppm water)	time (sec)	0	2715	6662	10609	14555	18501	22445	26394
	% 2,6-*trans*	0	4.7	7.9	9.8	11.1	12.0	12.6	13.2
area Naphthalene	5.4		306.7	306.8	308.3	308.4	308.9	309.3	308.7
area 2,6-*cis*	10.18		561.8	545.6	537.6	526.3	522.6	519	514.3
area 2,6-*trans*	10.42		27.8	46.8	58.3	65.5	71	75	78
Conc. 2,6-*cis*	(mol/L)		0.0661	0.0642	0.0630	0.0616	0.0611	0.0606	0.0602
Conc. 2,6-*trans*	(mol/L)		0.0033	0.0055	0.0068	0.0077	0.0083	0.0088	0.0091
ln [*trans* eq/*trans* eq-*trans* x]			0.0982	0.1712	0.2170	0.2473	0.2706	0.2879	0.3020
ln [*cis-cis* eq]			-3.4694	-3.5333	-3.5770	-3.6263	-3.6465	-3.6658	-3.6828
cis + *trans*	(mol/L)		0.0694	0.0697	0.0698	0.0693	0.0694	0.0693	0.0693

Table C.11 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.71 mM iron chloride in nitromethane at 60°C with various amounts of water

135-2 FeCl3 + 571ppm Water	time (sec)	0	52	2675	5306	7935	10563	13309	18447	23706	31585	47353
	% 2,6-*trans*	0	0.5	7.4	11.5	14.4	16.5	18.1	20.3	21.7	22.7	23.5
area Napthalene			644.6	650.2	647.8	644.4	645.6	647.0	647.1	647.5	645.8	644.5
area 2,6-*cis*			863.7	804.6	769.8	740.2	722.8	711.1	692.7	678.8	668.1	660.9
area 2,6-*trans*			4.6	64.3	100.3	124.2	142.6	157.1	176.4	187.7	196.3	203.1
Conc. 2,6-*cis*			0.0209	0.0193	0.0185	0.0179	0.0174	0.0171	0.0167	0.0163	0.0161	0.0160
Conc. 2,6-*trans*			0.0001	0.0015	0.0024	0.0030	0.0034	0.0038	0.0042	0.0045	0.0047	0.0049
cis + trans			0.0210	0.0208	0.0209	0.0209	0.0209	0.0209	0.0209	0.0208	0.0208	0.0209
ln [*trans* eq/ *trans* eq-*trans* x]			0.0101	0.1507	0.2472	0.3184	0.3747	0.4208	0.4872	0.5278	0.5621	0.5902
ln [*cis-cis* eq]			-4.6202	-4.7967	-4.8939	-4.9799	-5.0480	-5.0989	-5.1747	-5.2375	-5.2787	-5.3069

135-2 FeCl3 + 571ppm Water	time (sec)	76272	372809	517481	1235857	1282004	1284629	1287259	1289891	1292523	1295153
	% 2,6-*trans*	23.7	23.9	23.9	23.9	23.9	26.4	28.7	30.6	32.1	33.2
area Napthalene		644.3	637.8	633.8	645.4	634.8	651.7	639.1	643.1	646.0	645.4
area 2,6-*cis*		657.7	648.9	646.3	673.7	658.7	646.8	618.3	604.1	594.2	586.0
area 2,6-*trans*		204.7	203.9	203.3	211.4	207.2	232.0	249.4	266.2	280.3	291.7
Conc. 2,6-*cis*		0.0159	0.0158	0.0159	0.0162	0.0161	0.0154	0.0151	0.0146	0.0143	0.0141
Conc. 2,6-*trans*		0.0049	0.0050	0.0050	0.0051	0.0051	0.0055	0.0061	0.0064	0.0068	0.0070
cis + trans		0.0208	0.0208	0.0209	0.0213	0.0212	0.0210	0.0211	0.0211	0.0211	0.0212
ln [*trans* eq/ *trans* eq-*trans* x]		0.5969	0.6020	0.6047	0.6225	0.6194	0.7004	0.8031	0.8809	0.9515	1.0200
ln [*cis-cis* eq]		-5.3216	-5.3324	-5.3250	-5.2507	-5.2693	-5.4161	-5.5078	-5.6219	-5.7097	-5.7670

135-2 FeCl3 + 571ppm Water	time (sec)	1297783	1303045	1310938	1318825	1329348	1345122	1360894	1442660	1529470	1700370
	% 2,6-*trans*	34.1	35.5	36.8	37.5	38.0	38.4	38.5	38.6	38.7	38.7
area Napthalene		647.1	649.5	649.8	649.1	648.3	645.2	644.1	661.9	754.1	1137.7
area 2,6-*cis*		576.9	565.9	553.6	546.3	541.2	535.8	532.6	546.8	626.6	951.5
area 2,6-*trans*		299.1	311.7	322.3	327.8	331.7	333.5	333.3	344.1	395.1	600.1
Conc. 2,6-*cis*		0.0139	0.0136	0.0133	0.0131	0.0130	0.0129	0.0129	0.0129	0.0129	0.0130
Conc. 2,6-*trans*		0.0072	0.0075	0.0077	0.0079	0.0080	0.0080	0.0081	0.0081	0.0082	0.0082
cis + trans		0.0211	0.0210	0.0210	0.0210	0.0210	0.0210	0.0209	0.0209	0.0211	0.0212
ln [*trans* eq/ *trans* eq-*trans* x]		1.0610	1.1361	1.2096	1.2532	1.2867	1.3139	1.3170	1.3297	1.3517	1.3712
ln [*cis-cis* eq]		-5.8523	-5.9683	-6.0934	-6.1673	-6.2193	-6.2539	-6.2831	-6.2896	-6.2500	-6.2073

Table C.12 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.56 mM iron chloride in nitromethane with 571 ppm water at 60°C

			4/13/03 12:34pm									
135-3 FeCl3 + 1711ppm Water	time (sec)	0	1363	3990	6621	9248	11876	14505	19762	25020	32897	48670
	% 2,6-*trans*	0	6.7	14.1	18.4	21.0	22.8	23.9	25.1	25.6	25.9	26.1
area Napthalene			642.7	646.7	645.7	647.5	651.4	651.1	654.4	653.6	654.9	648.5
area 2,6-*cis*			805.7	743.5	707.6	684.6	672.5	663.3	654.8	650.3	648.9	644.0
area 2,6-*trans*			58.3	122.3	159.1	182.2	198.1	208.0	220.0	223.9	226.9	227.4
Conc. 2,6-*cis*			0.01944	0.017829	0.01699	0.016	0.016	0.016	0.016	0.015	0.015	0.015
Conc. 2,6-*trans*			0.00141	0.002933	0.00382	0.004	0.005	0.005	0.005	0.005	0.005	0.005
cis + trans			0.02085	0.020762	0.02082	0.021	0.021	0.021	0.021	0.021	0.021	0.021
ln [*trans* eq/ *trans* eq-*trans* x]			0.13684	0.310087	0.42676	0.505	0.560	0.599	0.642	0.660	0.670	0.682
ln [*cis*-*cis* eq]			-4.7746	-4.986532	-5.11688	-5.222	-5.296	-5.339	-5.400	-5.419	-5.434	-5.426

							Added 0.03ml Cat 4/28 8:40AM					
135-3 FeCl3 + 1711ppm Water	time (sec)		77586	374122	518794	1237172	1283316	1284629	1288575	1291207	1293837	1296469
	% 2,6-*trans*		26.1	26.2	26.1	26.2	27.4	30.2	32.7	34.6	36.0	37.2
area Napthalene			645.5	640.9	646.4	754.1	742.6	744.6	737.7	743.2	746.0	748.5
area 2,6-*cis*			639.2	634.8	639.5	753.7	732.6	700.6	672.9	658.9	647.8	636.5
area 2,6-*trans*			226.0	225.1	226.3	267.4	275.8	303.7	327.3	348.0	364.6	376.5
Conc. 2,6-*cis*			0.015	0.015	0.015	0.015	0.015	0.015	0.014	0.014	0.013	0.013
Conc. 2,6-*trans*			0.005	0.005	0.005	0.005	0.006	0.006	0.007	0.007	0.008	0.008
cis + trans			0.021	0.021	0.021	0.021	0.021	0.021	0.021	0.021	0.021	0.021
ln [*trans* eq/ *trans* eq-*trans* x]			0.680	0.684	0.680	0.693	0.742	0.856	0.982	1.079	1.168	1.235
ln [*cis*-*cis* eq]			-5.436	-5.435	-5.439	-5.404	-5.449	-5.629	-5.762	-5.897	-6.005	-6.125

135-3 FeCl3 + 1711ppm Water	time (sec)	1299098	1304360	1312254	1320141	1330662	1346436	1362209	1443974	1530788	1638594
	% 2,6-*trans*	38.0	39.4	40.5	41.1	41.5	41.7	41.9	42.0	42.0	42.0
area Napthalene		752.5	763.6	768.1	779.6	799.3	815.8	832.1	944.9	1223.1	2434.4
area 2,6-*cis*		632.7	626.3	618.1	620.5	631.2	637.9	652.4	743.9	987.0	2064.7
area 2,6-*trans*		388.1	406.5	419.9	432.8	447.9	457.2	470.4	538.7	714.7	1495.4
Conc. 2,6-*cis*		0.013	0.013	0.012	0.012	0.012	0.012	0.012	0.012	0.013	0.013
Conc. 2,6-*trans*		0.008	0.008	0.008	0.009	0.009	0.009	0.009	0.009	0.009	0.010
cis + trans		0.021	0.021	0.021	0.021	0.021	0.021	0.021	0.021	0.022	0.023
ln [*trans* eq/ *trans* eq-*trans* x]		1.299	1.388	1.473	1.526	1.561	1.561	1.595	1.628	1.736	2.010
ln [*cis*-*cis* eq]		-6.195	-6.366	-6.516	-6.613	-6.687	-6.789	-6.760	-6.718	-6.493	-6.141

Table C.13 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.55 mM iron chloride in nitromethane with 1711 ppm water at 60°C

15-2 DBMP +Al trifluoromethane sulphonate	time (sec)	0	1372	11868	30231	40728	127471				
	% 2,6-*trans*	0	0.3	0.4	0.5	0.5	0.6				
area Napthalene			560.80	559.40	561.10	564.30	578.60				
area 2,6-*cis*			963.20	958.70	967.90	972.10	982.50				
area 2,6-*trans*			3.20	4.20	4.80	4.50	5.50				
Conc. 2,6-*cis*			0.0239	0.0238	0.0240	0.0240	0.0236				
Conc. 2,6-*trans*			0.0001	0.0001	0.0001	0.0001	0.0001				
ln [*trans* eq/*trans* eq-*trans* x]			0.0066	0.0087	0.0100	0.0093	0.0111				
ln [*cis-cis* eq]			-4.2773	-4.2810	-4.2698	-4.2722	-4.2970				
cis + *trans*			0.0240	0.0239	0.0241	0.0241	0.0237				
		4/21/04 11:20am						Added 15C(DBMP in CH3NO2) @ 12:53pm			
16-1 AlOtf3 DBMP added after 1hr 33min+A	time (sec)	0	58	1372	2688	4005	5322	6639	7956	9273	10590
	% 2,6-*trans*	0	0.5	8.3	18.6	28.0	35.5	39.3	42.6	45.1	46.8
area Napthalene			567.80	570.70	564.90	531.60	566.40	540.10	541.60	546.80	551.90
area 2,6-*cis*			946.00	887.40	782.70	632.00	619.60	565.30	534.60	508.60	496.70
area 2,6-*trans*			4.50	80.60	178.90	245.90	341.40	366.40	397.00	417.70	437.30
Conc. 2,6-*cis*			0.0232	0.0216	0.0193	0.0165	0.0152	0.0146	0.0137	0.0129	0.0125
Conc. 2,6-*trans*			0.0001	0.0020	0.0044	0.0064	0.0084	0.0094	0.0102	0.0106	0.0110
ln [*trans* eq/*trans* eq-*trans* x]			0.0092	0.1787	0.4572	0.7678	1.1986	1.5419	1.8925	2.1636	2.5017
ln [*cis-cis* eq]			-4.3302	-4.4551	-4.6816	-5.0314	-5.2572	-5.3921	-5.5929	-5.8319	-5.9862
cis + *trans*			0.0233	0.0236	0.0237	0.0230	0.0236	0.0240	0.0239	0.0236	0.0235

16-1 AlOtf3 DBMP added after 1hr 33min+A	time (sec)	11906	13222	14537	15853	17169	18484	19801	21119	127649
	% 2,6-*trans*	48.0	48.8	49.4	49.7	49.9	50.1	50.2	50.3	50.4
area Napthalene		542.10	543.30	548.70	549.90	538.10	540.60	540.20	545.50	555.80
area 2,6-*cis*		483.80	475.80	470.30	467.10	463.10	462.10	459.90	457.10	436.20
area 2,6-*trans*		446.20	453.10	458.30	461.70	461.60	463.90	463.10	462.20	443.80
Conc. 2,6-*cis*		0.0124	0.0122	0.0119	0.0118	0.0120	0.0119	0.0118	0.0117	0.0109
Conc. 2,6-*trans*		0.0114	0.0116	0.0116	0.0117	0.0119	0.0119	0.0119	0.0118	0.0111
ln [*trans* eq/*trans* eq-*trans* x]		3.0721	3.3898	3.4344	3.6048	5.1035	5.1598	5.0023	4.0017	2.5925
ln [*cis-cis* eq]		-6.0288	-6.1301	-6.2569	-6.3143	-6.2318	-6.2739	-6.2996	-6.4066	-7.0000
cis + *trans*		0.0239	0.0238	0.0235	0.0235	0.0239	0.0238	0.0238	0.0234	0.0220

Table C.14 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.83 mM aluminium trifluoromethanesulphonate (15-2) and 1.6 mM aluminium trifluoromethanesulphonate (16-1 with 0.16 mM 2,6-di-*tert*-butyl-4-methylpyridine added after 1 hr 33 min) in nitromethane at 40°C

	4/23/04 12:35pm				Added 15C(DBMP in CH3NO2) @ 1:20pm					
16-2 AlOtf3 DBMP added after 45min+Al trif time (sec)	0	55	1365	2678	3993	5308	6623	7938	9252	10567
% 2,6-*trans*	0	0.5	5.9	13.7	16.9	20.8	24.4	27.6	30.5	32.9
area Napthalene		571.50	564.60	558.10	540.50	539.70	539.00	538.30	538.50	538.70
area 2,6-*cis*		956.60	906.70	828.50	768.60	733.10	698.40	667.50	626.00	617.30
area 2,6-*trans*		4.80	56.60	131.00	156.30	192.10	225.40	254.90	274.50	303.30
Conc. 2,6-*cis*		0.0233	0.0223	0.0206	0.0198	0.0189	0.0180	0.0172	0.0162	0.0159
Conc. 2,6-*trans*		0.0001	0.0014	0.0033	0.0040	0.0049	0.0058	0.0066	0.0071	0.0078
ln [*trans* eq/*trans* eq-*trans* x]		0.0098	0.1235	0.3174	0.4080	0.5317	0.6627	0.7955	0.8931	1.0565
ln [*cis-cis* eq]		-4.3220	-4.3959	-4.5431	-4.6283	-4.7233	-4.8264	-4.9280	-5.0892	-5.1273
cis + *trans*		0.0234	0.0237	0.0239	0.0238	0.0238	0.0238	0.0238	0.0233	0.0238

16-2 AlOtf3 DBMP added after 45min+Al trif time (sec)	11883	13198	14514	17145	19779	23731	26365	29000
% 2,6-*trans*	35.1	36.9	38.6	41.2	43.2	45.4	46.5	47.3
area Napthalene	537.20	536.30	537.60	534.30	537.30	535.70	537.70	537.60
area 2,6-*cis*	593.60	580.40	564.40	536.60	522.20	499.60	490.50	483.60
area 2,6-*trans*	320.60	340.00	354.20	375.90	397.70	415.90	425.80	434.00
Conc. 2,6-*cis*	0.0154	0.0150	0.0146	0.0140	0.0135	0.0130	0.0127	0.0125
Conc. 2,6-*trans*	0.0083	0.0088	0.0092	0.0098	0.0103	0.0108	0.0110	0.0112
ln [*trans* eq/*trans* eq-*trans* x]	1.1760	1.3263	1.4413	1.6882	1.9492	2.2979	2.4952	2.7390
ln [*cis-cis* eq]	-5.2281	-5.2890	-5.3824	-5.5306	-5.6513	-5.8203	-5.9207	-5.9886
cis + *trans*	0.0237	0.0239	0.0238	0.0237	0.0238	0.0238	0.0237	0.0237

16-2 AlOtf3 DBMP added after 45min+Al trif time (sec)	32951	36902	40854	44806	48756	55334	63212	128841
% 2,6-*trans*	48.2	48.8	49.2	49.6	49.8	50.0	50.2	50.4
area Napthalene	536.80	535.40	536.00	534.70	533.80	530.50	533.80	524.00
area 2,6-*cis*	474.50	467.40	464.30	461.00	456.30	451.70	450.50	437.60
area 2,6-*trans*	441.30	445.50	450.30	452.80	452.00	451.60	454.00	444.70
Conc. 2,6-*cis*	0.0123	0.0121	0.0120	0.0120	0.0119	0.0118	0.0117	0.0116
Conc. 2,6-*trans*	0.0114	0.0116	0.0117	0.0118	0.0118	0.0118	0.0118	0.0118
ln [*trans* eq/*trans* eq-*trans* x]	3.0473	3.3269	3.6265	3.9726	3.9682	4.2920	4.2291	4.0924
ln [*cis-cis* eq]	-6.0792	-6.1480	-6.1929	-6.2210	-6.2738	-6.2988	-6.3573	-6.4308
cis + *trans*	0.0237	0.0237	0.0237	0.0238	0.0237	0.0237	0.0236	0.0234

Table C.15 GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.6 mM aluminium trifluoromethanesulphonate (16-2 with 0.16 mM 2,6-di-*tert*-butyl-4-methylpyridine added after 45 min) in nitromethane at 40°C

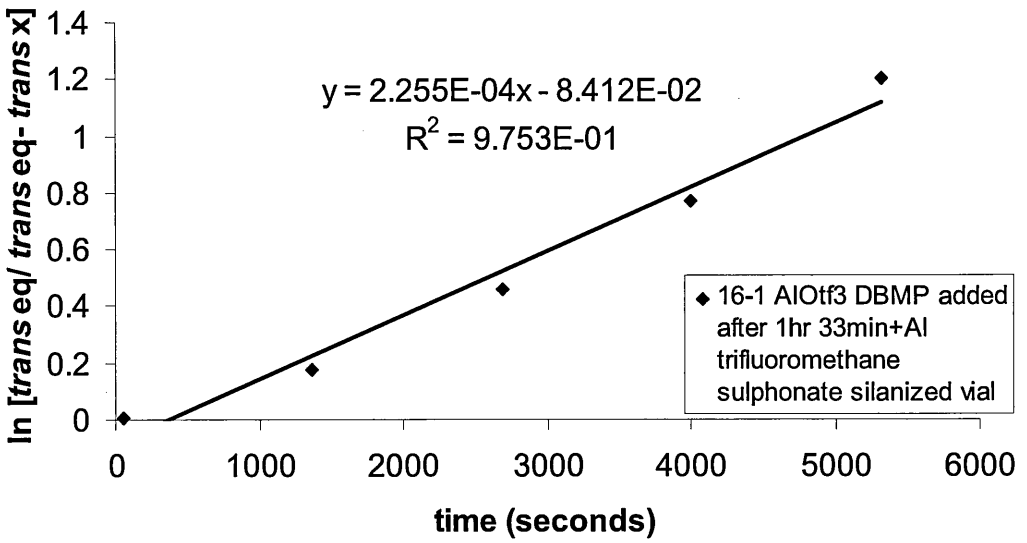


Figure C.9 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by1.6 mM aluminium trifluoromethanesulphonate in nitromethane at 40°C

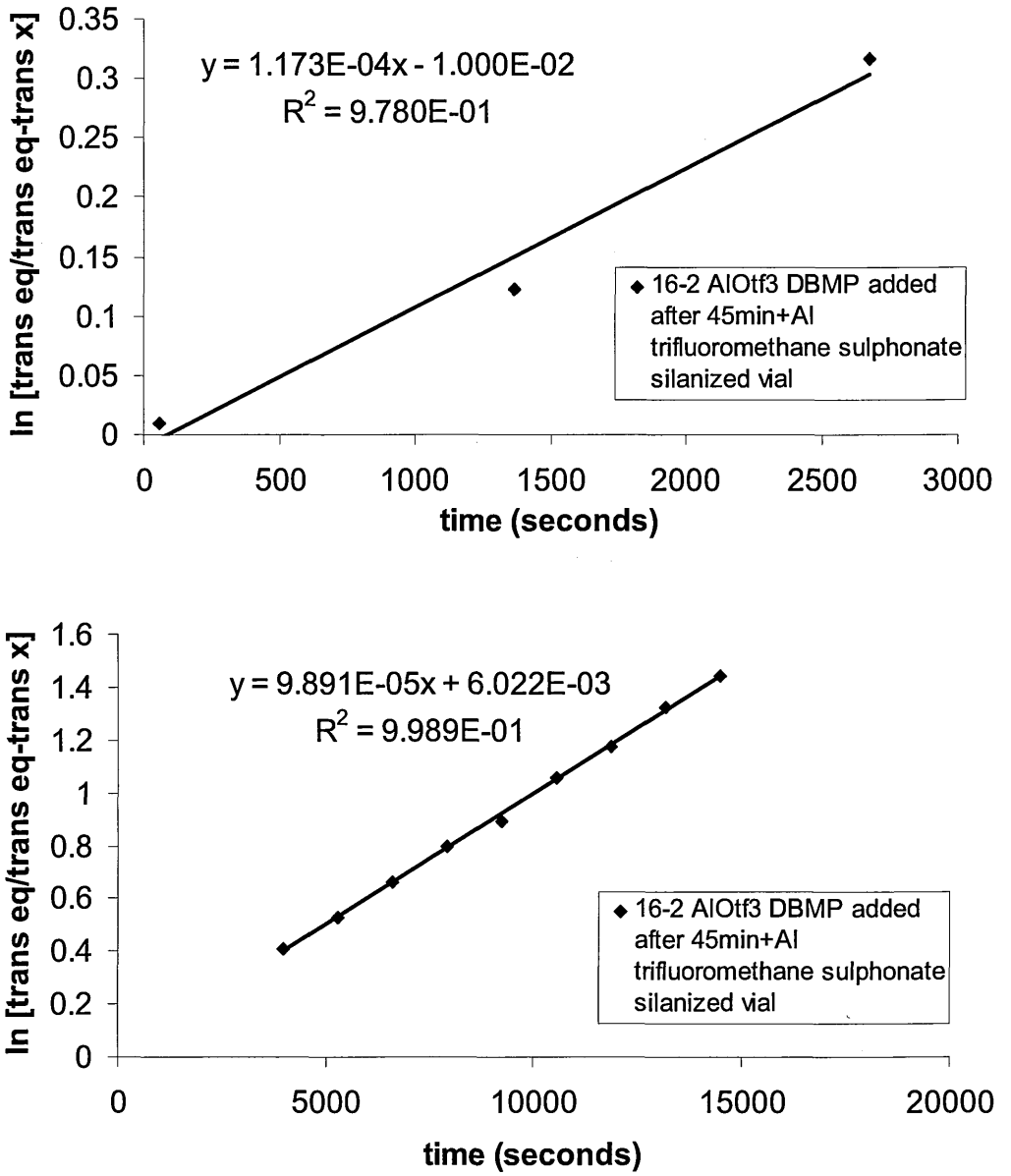


Figure C.10 Reaction rate constant calculated from GC data for the interconversion reaction of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 0.16 mM aluminium trifluoromethanesulphonate (first 45 min, top figure) where 2,6-di-*tert*-butyl-4-methylpyridine was added after 45 min (bottom figure) in nitromethane at 40°C

5/20/04 12:50pm

17-1 Al trifluoromethane sulphonate silanize time (sec)	0	92	2719	5350	7980	10611	13241	15872
% 2,6-*trans*	0	1.2	25.5	38.4	44.5	47.5	49.0	49.7
area Napthalene		571.50	507.50	561.70	569.80	571.60	567.90	564.20
area 2,6-*cis*		951.90	585.00	569.30	528.10	504.20	488.40	480.50
area 2,6-*trans*		11.90	200.70	354.40	424.10	456.50	468.70	475.00
Conc. 2,6-*cis*		0.0232	0.0160	0.0141	0.0129	0.0123	0.0120	0.0118
Conc. 2,6-*trans*		0.0003	0.0055	0.0088	0.0103	0.0111	0.0115	0.0117
ln [*trans* eq/*trans* eq-*trans* x]		0.0244	0.6129	1.3132	1.9832	2.5947	3.1294	3.7076
ln [*cis-cis* eq]		-4.3307	-5.1115	-5.4988	-5.8478	-6.0905	-6.2362	-6.2974
cis + *trans*		0.0234	0.0215	0.0229	0.0232	0.0234	0.0234	0.0235

17-1 Al trifluoromethane sulphonate silanize time (sec)	18506	21142	23777	26414	29049	39593
% 2,6-*trans*	50.0	50.2	50.3	50.4	50.4	50.4
area Napthalene	570.10	564.30	565.20	569.50	567.90	564.40
area 2,6-*cis*	478.80	474.50	473.20	476.10	475.00	471.30
area 2,6-*trans*	479.50	479.00	478.90	482.90	482.20	479.00
Conc. 2,6-*cis*	0.0117	0.0117	0.0116	0.0116	0.0116	0.0116
Conc. 2,6-*trans*	0.0117	0.0118	0.0118	0.0118	0.0118	0.0118
ln [*trans* eq/*trans* eq-*trans* x]	3.6696	4.1046	4.0026	4.0432	4.1226	4.0941
ln [*cis-cis* eq]	-6.3907	-6.3823	-6.4127	-6.4232	-6.4196	-6.4314
cis + *trans*	0.0234	0.0235	0.0234	0.0234	0.0234	0.0234

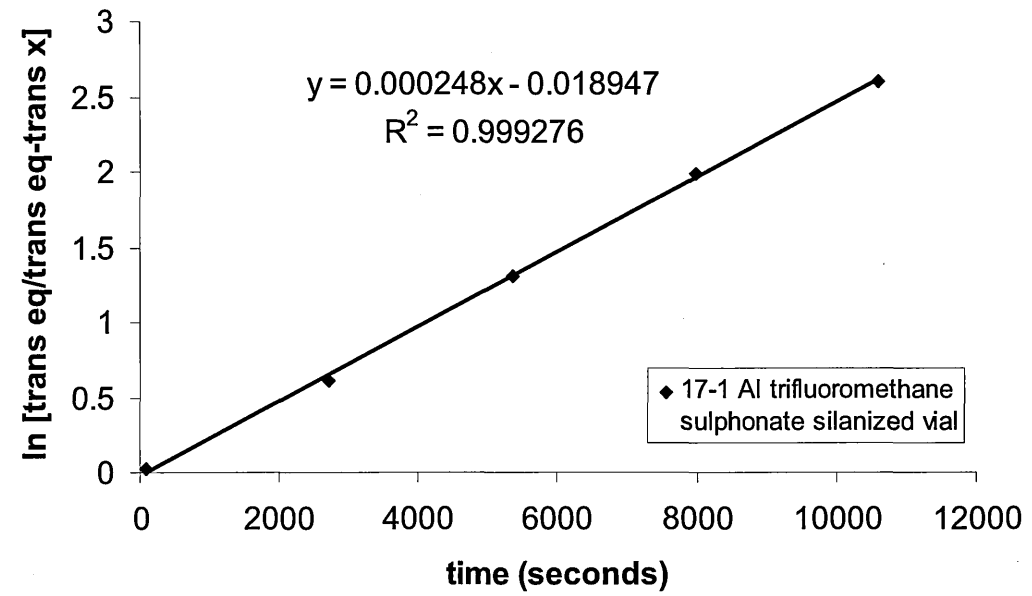
Table C.16 GC data for the interconversion reaction of 21 mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.6 mM aluminium trifluoromethanesulphonate in nitromethane at 40°C

	5/20/04 12:50pm								
17-2 DBMP +Al trifluoromethane sulphonate	time (sec)	0	1404	4035	6665	9295	11926	14555	17187	19824
	% 2,6-*trans*	0	7.6	20.0	28.7	34.9	39.2	42.4	44.6	46.1
area Napthalene			574.00	564.00	566.10	571.10	566.70	568.00	566.90	565.50
area 2,6-*cis*			890.80	768.30	683.90	630.30	567.10	555.90	531.10	516.90
area 2,6-*trans*			72.80	191.80	275.70	337.70	366.10	408.40	426.70	442.70
Conc. 2,6-*cis*			0.0216	0.0189	0.0168	0.0153	0.0139	0.0136	0.0130	0.0127
Conc. 2,6-*trans*			0.0018	0.0047	0.0068	0.0082	0.0090	0.0100	0.0105	0.0109
ln [*trans* eq/*trans* eq-*trans* x]			0.1589	0.5009	0.8308	1.1556	1.3803	1.7903	2.0565	2.3756
ln [*cis*-*cis* eq]			-4.4587	-4.7172	-4.9913	-5.2316	-5.5433	-5.6247	-5.8006	-5.9112
cis + *trans*			0.0233	0.0237	0.0236	0.0236	0.0229	0.0236	0.0235	0.0236

17-2 DBMP +Al trifluoromethane sulphonate	time (sec)	22460	25095	27731	33003	38275	40912
	% 2,6-*trans*	47.3	48.1	48.7	49.5	49.9	50.0
area Napthalene		567.00	567.20	559.20	565.40	563.60	565.70
area 2,6-*cis*		507.00	497.30	488.70	482.90	478.50	476.70
area 2,6-*trans*		454.40	461.20	463.60	472.80	476.20	476.90
Conc. 2,6-*cis*		0.0124	0.0122	0.0122	0.0119	0.0118	0.0117
Conc. 2,6-*trans*		0.0111	0.0113	0.0115	0.0116	0.0117	0.0117
ln [*trans* eq/*trans* eq-*trans* x]		2.6388	2.8493	3.2331	3.4701	3.8618	3.7622
ln [*cis*-*cis* eq]		-6.0189	-6.1237	-6.1419	-6.2792	-6.3175	-6.3676
cis + *trans*		0.0236	0.0235	0.0237	0.0235	0.0236	0.0234

	5/21/04 1:10pm									
17-3 DBMP +Al trifluoromethane sulphonate	time (sec)	0	97	1407	2720	13229	39545	65849	92141	118477
	% 2,6-*trans*	0	0.9	0.5	0.4	0.4	0.5	0.6	0.7	0.8
area Napthalene			556.40	557.20	557.10	557.10	551.60	550.10	550.40	548.70
area 2,6-*cis*			940.20	951.50	952.00	955.80	942.00	938.70	935.00	938.00
area 2,6-*trans*			8.50	4.70	4.00	4.00	4.80	5.80	6.90	7.90
Conc. 2,6-*cis*			0.0235	0.0237	0.0238	0.0239	0.0237	0.0237	0.0236	0.0238
Conc. 2,6-*trans*			0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0002
ln [*trans* eq/*trans* eq-*trans* x]			0.0179	0.0098	0.0084	0.0084	0.0101	0.0123	0.0146	0.0168
ln [*cis*-*cis* eq]			-4.3055	-4.2873	-4.2860	-4.2792	-4.2871	-4.2885	-4.2963	-4.2854
cis + *trans*			0.0237	0.0239	0.0239	0.0240	0.0239	0.0239	0.0238	0.0240

Table C.17 GC data for the interconversion reaction of 21mM 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.6 mM aluminium trifluoromethanesulphonate with 0.69 mM (17-2) or 2.1mM (17-3) 2,6-di-*tert*-butyl-4-methylpyridine in nitromethane at 40°C



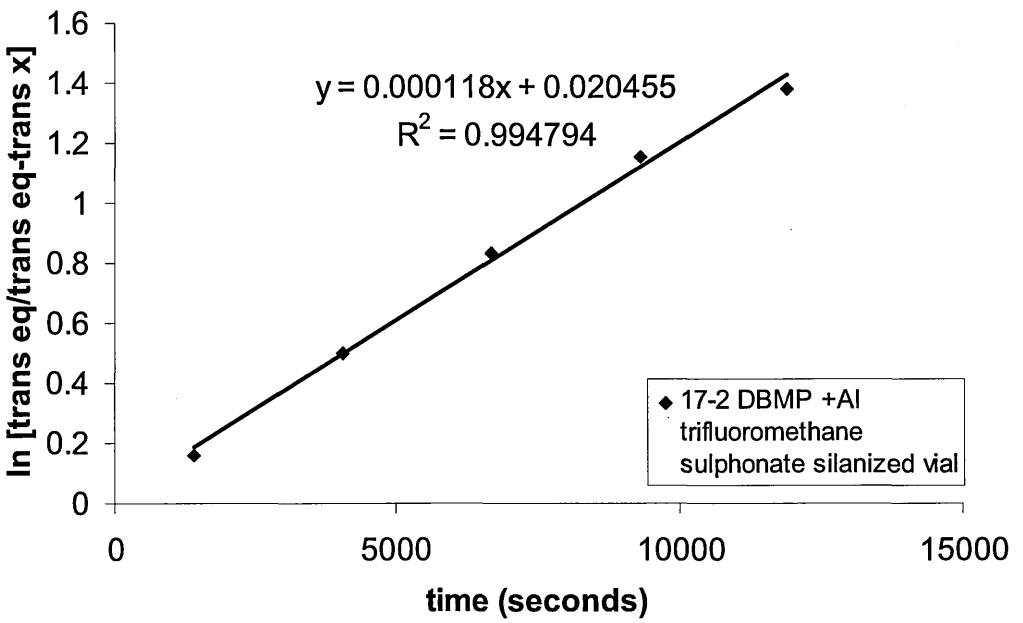


Figure C.11 Reaction rate constant calculated from GC data for the interconversion reaction of of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane catalysed by 1.6 mM aluminium trifluoromethanesulphonate (where 17-2 also contains 0.69 mM 2,6-di-*tert*-butyl-4-methylpyridine) in nitromethane at 40°C